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(54) **OXIRANE (ETHYLENE OXIDE) POLYURETHANE COATINGS**

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C08G 18/10	(2006.01)
C08G 65/32	(2006.01)
C08G 65/332	(2006.01)
C08G 18/08	(2006.01)
C08G 18/48	(2006.01)
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C08G 18/76	(2006.01)
C09D 175/08	(2006.01)
C08G 18/40	(2006.01)
C08G 18/42	(2006.01)

(52) **U.S. Cl.**

CPC ***C08G 18/0823*** (2013.01); ***C08G 18/0866*** (2013.01); ***C08G 18/4018*** (2013.01); ***C08G 18/4238*** (2013.01); ***C08G 18/4808*** (2013.01); ***C08G 18/4833*** (2013.01); ***C08G 18/4854*** (2013.01); ***C08G 18/6692*** (2013.01); ***C08G 18/73*** (2013.01); ***C08G 18/7671*** (2013.01); ***C09D 175/08*** (2013.01); *C08G 2210/00* (2013.01)

(58) **Field of Classification Search**

CPC C08G 18/2845; C08G 18/4244; C08G 18/4247

See application file for complete search history.

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(57) **ABSTRACT**

The present invention relates to hydrophilic, i.e., water loving coatings (hereafter referred to as "WLC"). Polyurethane epoxy alkylene oxide coatings usable as coatings on for example, medical devices are a preferred WLC.

6 Claims, No Drawings

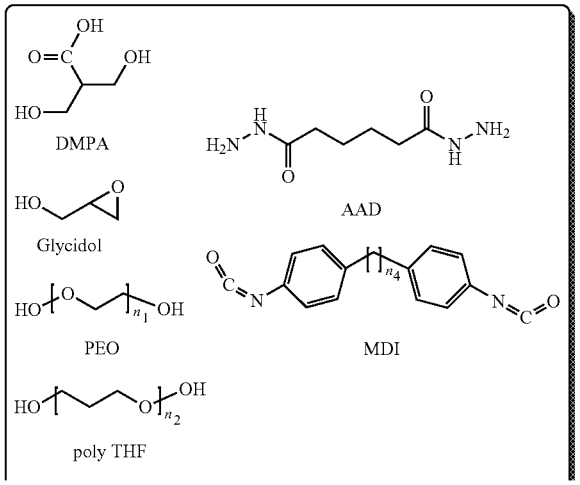
OXIRANE (ETHYLENE OXIDE) POLYURETHANE COATINGS

BACKGROUND OF THE INVENTION

Hydrophilic, i.e., water loving coatings (hereafter referred to as "WLC") are a utilitarian chemistry that may be used for hydrophilic and hydrophobic polyurethane epoxies as a replacement of isocyanate-based coatings on, for example, medical devices. WLC chemistry is attractive since prior art isocyanates-based coating compositions and coatings that may be used present possible health concerns. Another concern, with isocyanates, is the isocyanate sensitivity to water which reacts therewith to evolve carbon dioxide. That side reaction produces a very rough coating due to micro roughness when carbon dioxide exits the coating forming small pin holes. However, once the isocyanate is end capped to form polyurethane epoxy (glycidyl carbamate) in accordance with this invention, reactions with water and off gassing are no longer a concern and health concerns are significantly reduced. The use of WLC chemistry, in medical devices, and other coating areas, is thusly very attractive particularly for medical device applications.

SUMMARY OF THE INVENTION

WLC synthesis reactions can be optimized generally by running at lower temperatures which tends to reduce side reactions. Reaction order is also a very important consideration in WLC development. In the case of oxirane polyurethane-based WLC's the methylenebisdiisocyanate (MDI) should be either a liquid or a melted solid before polyol additions and that adipic acid dihydrazide is fully reacted before adding dibutyltin dilaurate catalyst and glycidol. Adding glycidol too early may result in amine reactions with glycidol, and addition of catalyst too early may alter the chain extending network and form a less desirable coating. WLC glycidyl(oxirane functionality) termination has shown an increase in coating adhesive and cohesive strength.



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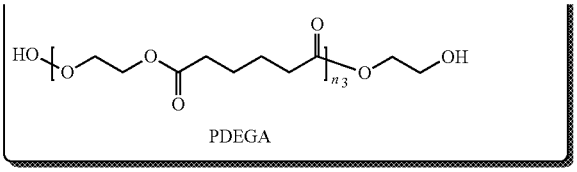


In the above formulae:

"n_1", relating to PEO, falls in the range of about 500 to about 45,000 or higher;

"n_2", relating to polyTHF, falls in the range of about 3 to about 600 or higher;

"n_3", relating to PDEGA, falls in the range of about 2 to about 60,000 or higher; and

"n_4" is lower alkylene, n_4 falling in the range of 1 to about 4.

Note that the n_4 alkylene group optionally couples other isocyanate moieties as is noted below.

1. Glycidol, PEO (polyethylene oxide), dimethylol propionic acid (DMPA), polytetrahydrofuran (polyTHF), and poly [di(ethylene glycol)adipate] (PDEGA hydroxyl) can react with methylenebisdiisocyanate for chain extension.
2. Adipic acid dihydrazide (AAD) reacts with isocyanate for chain extension.
3. End group is terminated with glycidol for glycidyl functionality.
4. Reaction kinetics are faster with an aromatic group next to isocyanate.

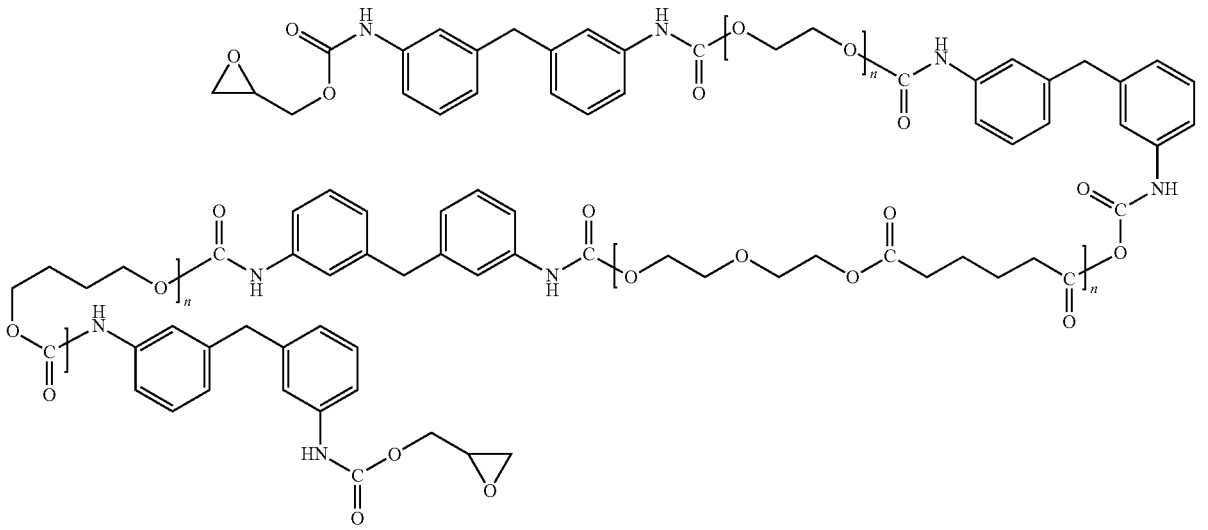
The monomers and oligomers (including the genericized polymer constituents) and synthetic route noted about was used to produce coatings/compositions of this invention.

Side reaction free reaction scheme to terminate with epoxy end groups and minimize side reactions.

The terminal oxirane polyurethane chemistry coatings of this invention primary reactions that make up the polyurethane coatings of this invention are listed below:

1. Terminal Oxirane Polyurethane Reactive Coating Compositions are an extremely lubricious durable coating that contains both hard and soft segments. This structure contains polyurethane and epoxy groups. This is a modified aqueous and solvent soluble material to increase physical crosslinks via hydrogen bonding. This structure relies on physical crosslinks for strength through hard segment domains. The hard segments contain aromatic groups, which also stack by pi-bond interactions. "Hard segments" as the term is used herein means substantially crystalline.

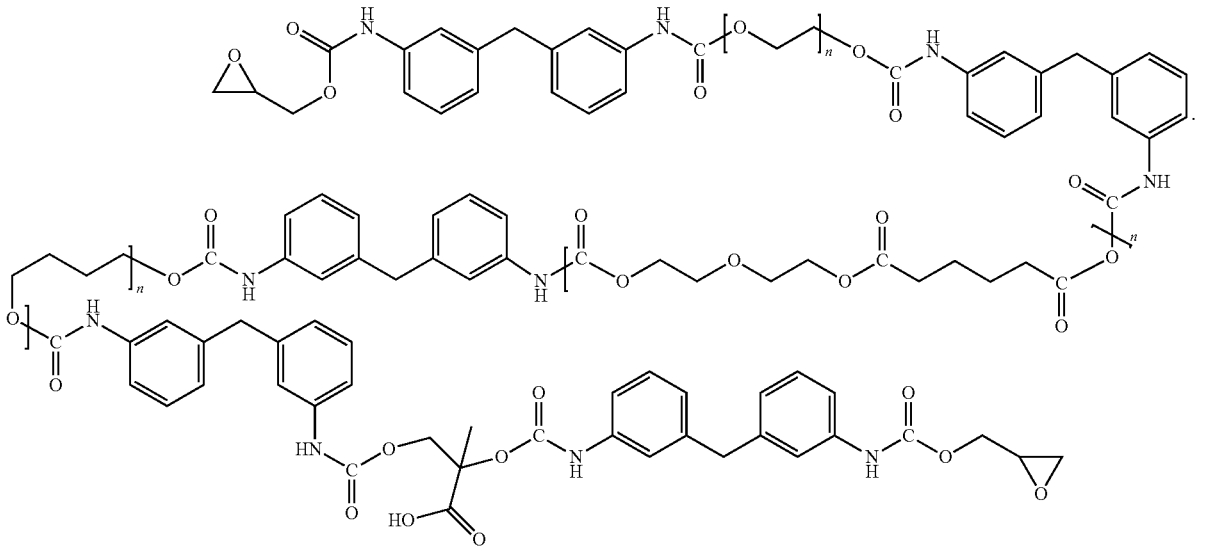
(I.)



2. Terminal a Composition Comprising Epoxy Urethane Ester Carboxylic Acid Alkylene Oxide Reactive Coating Compositions

This example describes the preparation of an inventive water-loving coating (WLC) Epoxy urethane ester carboxylic acid alkylene oxide reactive coating compositions. A 500 mL four neck reaction kettle with condenser, nitrogen inlet and model Gemini J-KEM temperature controller, mechanical stirrer, and heating mantel was used for resin synthesis. 16.8 g of methylenebisdiisocyanate (MDI)>99.0% was charged to the reactor. The temperature was held at 40 degree C. for 40 minutes for solid softening. Next, 62.5 g of Poly[di(ethylene glycol)adipate] average M_n~2,500, 72.5 g of Poly(tetrahydrofuran) average M_n~2,900, and 3.35 g of 2,2-Bis(hydroxymethyl)propionic acid 98% was added, in the following order and homogenized by stirring for 5 minutes at 40.degree. C. To this homogenized mixture 150 grams of Poly(ethylene oxide) average M_v 100,000, powder was added immediately following the addition of 1-Methyl-2-pyrrolidinone anhydrous, 99.5%. The solution homogenized by mixing thoroughly for 40 minutes. Four drops Dibutyltin dilaurate 95% were added drop wise and the reaction mixture was held at 40 degrees C. for one hour. After one hour 3.7 grams glycidol were added and the temperature was held overnight until reaction completion.

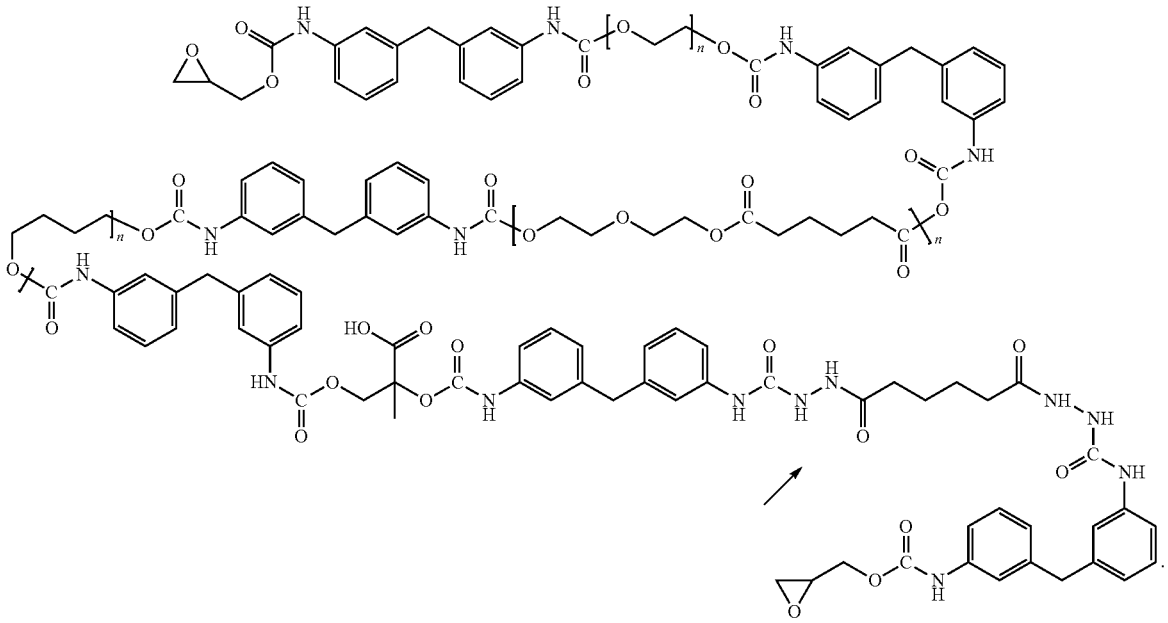
II



3. Terminal Oxirane Polyurethane Urea Chain Extender/(No Addition of Water).

Reactive Coating Compositions are an extremely lubricious durable coating that contains both hard and soft segments. The structure contains polyurethane, urea and epoxy groups. This is a modified aqueous and solvent soluble material that employs urea formation to increase physical crosslinks via hydrogen bonding. Carboxylic acid functionality in the polymer backbone and glycidol end groups add crosslinking. The epoxy end groups help with adhesion and cohesive strength. This structure relies on crosslinks much like the polyurethane epoxy but contains a chain extender based off adipic acid dihydrazide.

III

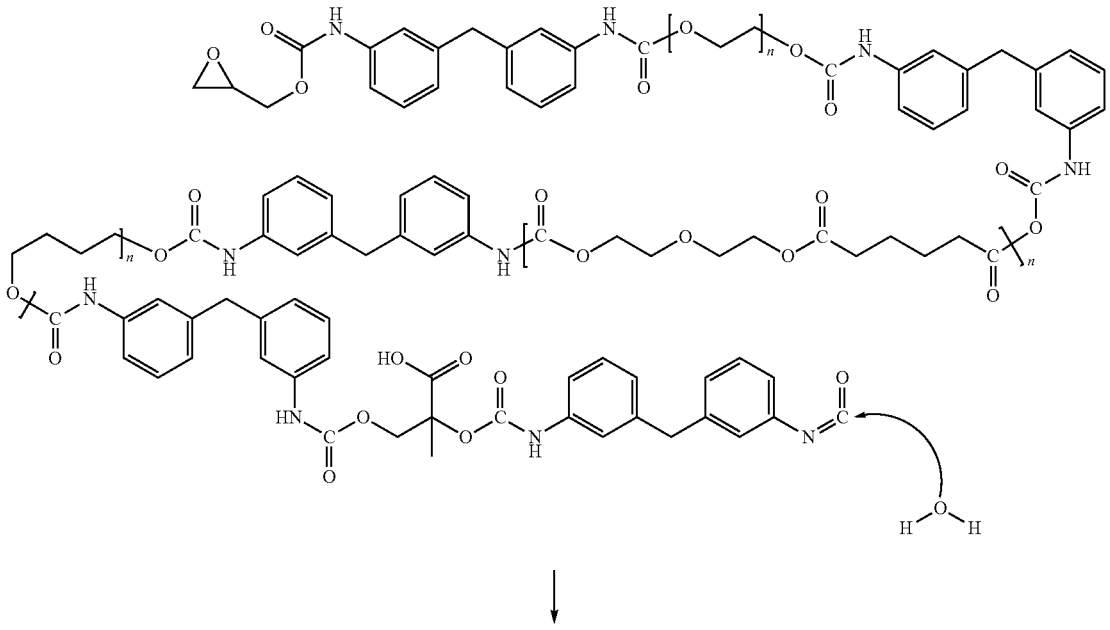


4. Terminal Oxirane Polyurethane Urea Chain Extender/(Water Excess).

Reactive Coating Compositions are an extremely lubricious durable coating that contains both hard and soft segments i.e., crystalline and amorphous segments. This structure contains polyurethane, urea and epoxy groups. This is a modified aqueous and solvent soluble material employs urea formation to increase physical crosslinks via hydrogen bonding. Carboxylic acid functionality in the polymer backbone and glycidol end groups add crosslinking, the reaction of isocyanate forms an unstable carbamic acid that forms an amine. The amine quickly reacts with isocyanate functionality to form a urea.

Water functionality reacts with excess MDI isocyanate to release CO_2 and form an amine. The amine functionality reacts with excess isocyanate to form additional urea linkages. The water/amine reaction is highly, physically crosslink the system and enhance its mechanical properties. The active hydrogen of the secondary amine can further react with excess isocyanate to slightly crosslink the system. The combination of urea, and polyurethane hard segments and glycidol functionalities lead to a superior crosslinking system.

IV



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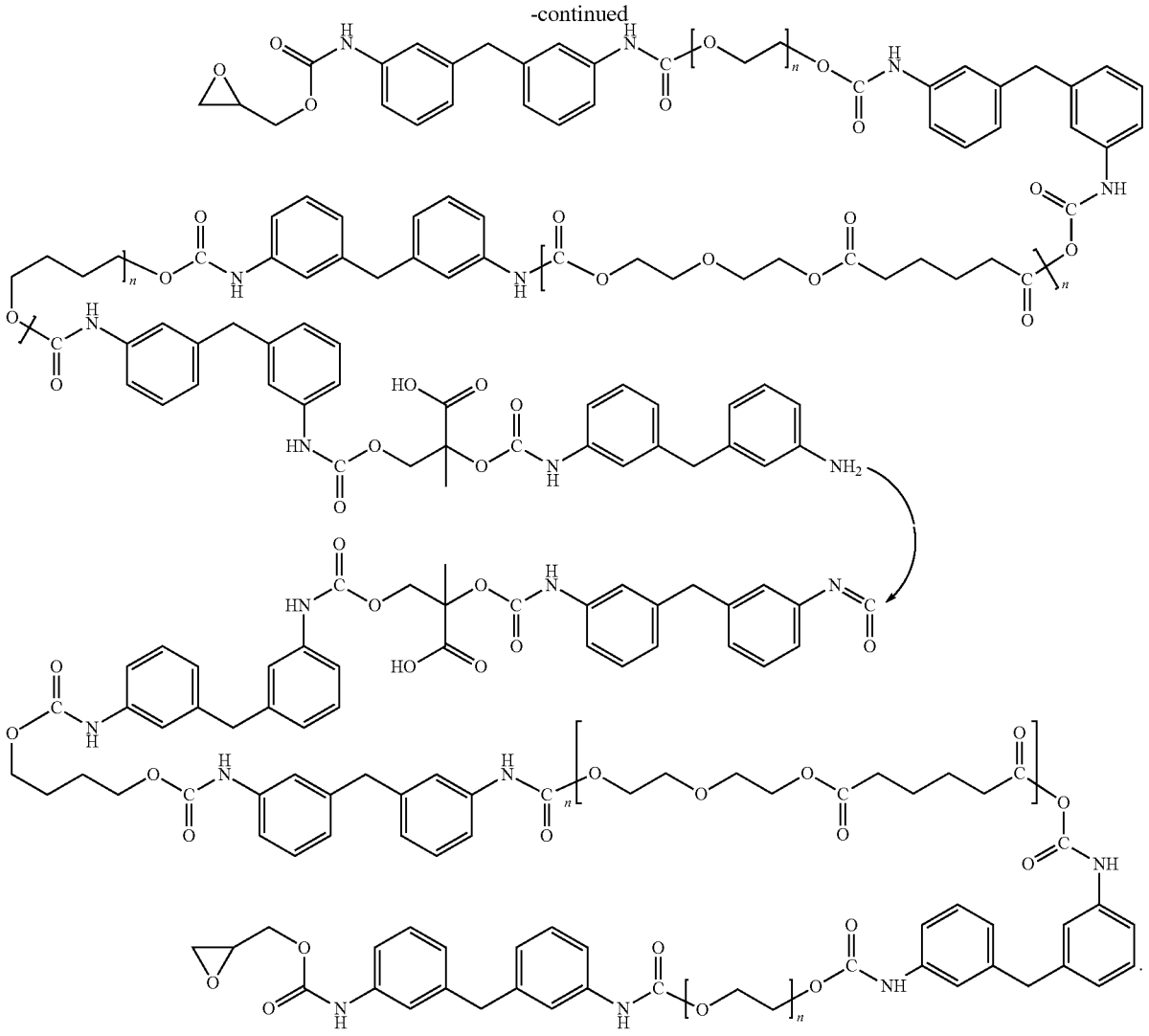


Water reactions with isocyanate to form urea

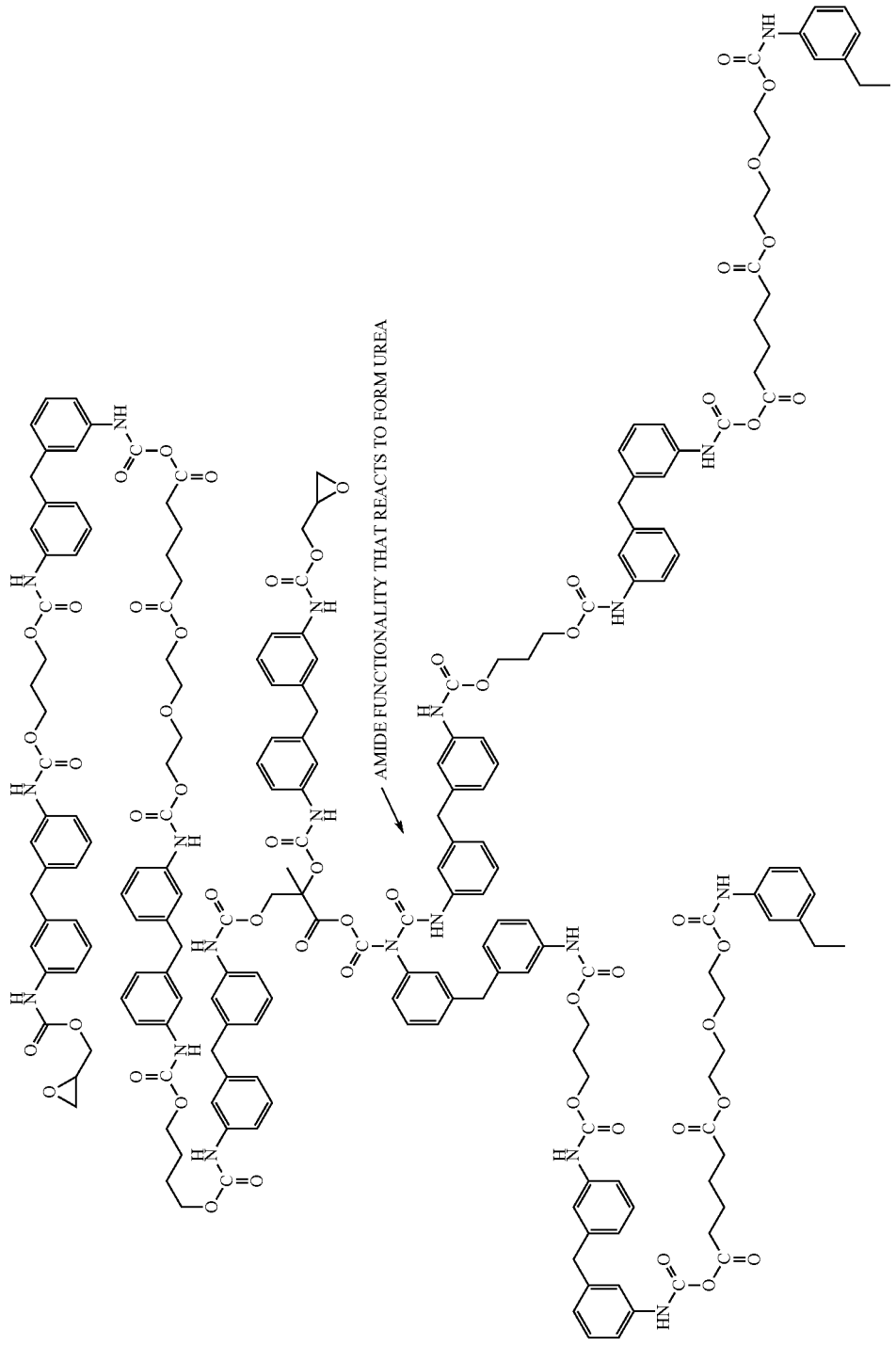
5. Terminal Oxirane Polyurethane Amide/Amide Urea/(No Addition of Water).

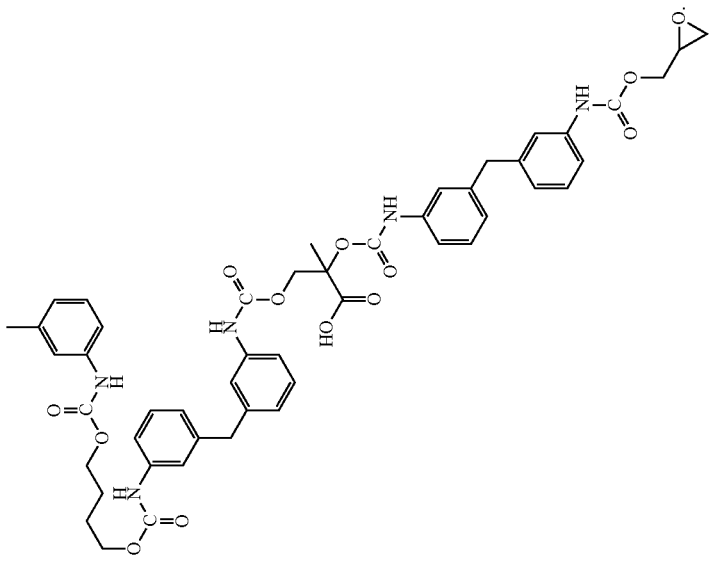
Reactive Coating Compositions are an extremely lubricious durable coating that contains both hard and soft segments. This is structure contains polyurethane, urea, amide (amide to form urea) and epoxy groups. This is a modified aqueous and solvent soluble material employs amide formation that may undergo additional reactions to form urea. Urea and hard segments yield an increase in hydrogen bonding for physical crosslinks, carboxylic acid functionality in the polymer backbone and glycidol end groups add crosslinking. Amide functionality can continue to react with isocyanate to form urea. This crosslinking system helps increase durability of the basecoat.

Isocyanate Reaction with Amide to Form Crosslinked Urea

For example, DMPA was used to construct the polymer backbone for the introducing carboxylic acid functionality. This functionality reacts with excess MDI isocyanate around 80 C to form an amide bond. The amide reaction is to slightly cross-link the system and increase its mechanical properties. The active hydrogen of the amide functionally can further react with excess isocyanate to form urea. The combination of amide, urea, and polyurethane hard segments and glycidol functionalities lead to a superior crosslinking system.

v





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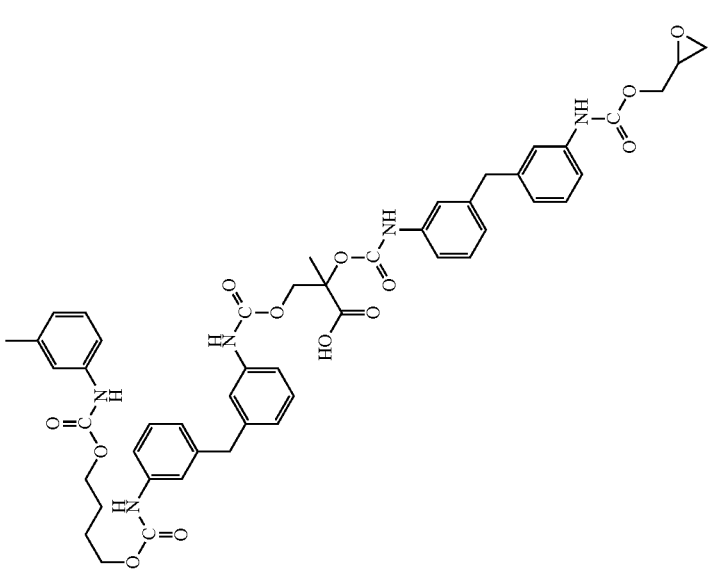

Isocyanate Reaction with Amide to Form Crosslinked Urea Examples 46-48 illustrate this aspect of the invention.

For example, DMPA was used to construct the polymer backbone for the introducing carboxylic acid functionality. This functionality reacts with excess MDI isocyanate around 80 C to form an amide bond. The amide reaction is to slightly crosslink the system and increase mechanical properties. The active hydrogen of amide can further react with excess isocyanate to form urea. The combination of amide, urea, and polyurethane hard segments and glycidol functionalities lead to a superior crosslinking system.

The following references, patents, and patent applications are incorporated by reference herein in their entireties.

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20110021657	Kocher, Hydrophilic polyurethane solutions
20110021696	Kocher et al., Hydrophilic polyurethane dispersions

Also, specifically incorporated by reference herein in its entirety is applicant's in concurrently filed patent application Ser. No. 13/834,810, entitled "Modified Hyaluronate Hydrophilic Compositions, Coatings and Methods."

DETAILED DESCRIPTION

Examples of Composition 1

Example 1

This example describes the preparation of an inventive water loving coating (WLC) glycidyl carbamate dispersion (E-1). A 500 mL four neck reaction kettle with condenser, nitrogen inlet and model Gemini J-KEM temperature controller, mechanical stirrer, and heating mantel was used for resin synthesis. 9.375 g of 4,4'-Methylenebis(phenyl isocyanate) 98% was charged to the reactor. The temperature was held at 40° C. for 40 minutes for solid softening. Next, 4.925 g of Poly[di(ethylene glycol)adipate] average M_n~500, 27.25 g of Poly(tetrahydrofuran) average M_n~2,900, was added, in the following order and homogenized by stirring for 5 minutes at 40° C. To this homogenized mixture 53.57 g of Poly(ethylene oxide) average M_v 100,000, powder was added immediately following the addition of 100 g of 1-Methyl-2-pyrrolidinone anhydrous, 99.5%. The solution homogenized by mixing thoroughly for 40 minutes. One drop Dibutyltin dilaurate 95% were added drop wise and the reaction mixture was held at 40° C. for one hour. After one hour 2.8 grams glycidol were added and the temperature was held overnight until reaction completion.

Example 1 (E-1)	grams	eq. Wt	moles
4,4'-Methylenebis(phenyl isocyanate)	9.375	125	0.075
Poly [di(ethylene glycol) adipate] average M_n ~500	4.925	250	0.0197
Poly(tetrahydrofuran) average M_n ~2,900	27.25	1450	0.018793
Poly (ethylene oxide) average M_v 100,000	53.57	50000	0.001071
glycidol	2.8	74	0.037838
			0.077402

Example 2

This example describes the preparation of an inventive water loving coating (WLC) glycidyl carbamate dispersion (E-2). A 500 mL four neck reaction kettle with condenser, nitrogen inlet and model Gemini J-KEM temperature controller, mechanical stirrer, and heating mantel was used for resin synthesis. 4.787 g of 4,4'-Methylenebis(phenyl isocyanate) 98% was charged to the reactor. The temperature was held at 40° C. for 40 minutes for solid softening. Next, 27.423 g of Poly(tetrahydrofuran) average M_n~2,900, was added, in the following order and homogenized by stirring for 5 minutes at 40° C. To this homogenized mixture 53.57 g of Poly(ethylene oxide) average M_v 100,000, powder was added immediately following the addition of 50 g of 1-Methyl-2-pyrrolidinone anhydrous, 99.5%. The solution homogenized by mixing thoroughly for 40 minutes. One drop of Dibutyltin dilaurate 95% were added drop wise and the reaction mixture was held at 40° C. for one hour. After one hour 1.8 grams glycidol were added and the temperature was held overnight until reaction completion.

Example 2 (E-2)	grams	eq. Wt	moles
4,4'-Methylenebis(phenyl isocyanate)	4.787	125	0.038296
Poly(tetrahydrofuran) average M_n ~2,900	27.423	1450	0.018912
Poly (ethylene oxide) average M_v 100,000	53.57	50000	0.001071
glycidol	1.8	74	0.024324
			1.044308

Example 3

This example describes the preparation of an inventive water loving coating (WLC) glycidyl carbamate dispersion (E-3). A 500 mL four neck reaction kettle with condenser, nitrogen inlet and model Gemini J-KEM temperature controller, mechanical stirrer, and heating mantel was used for resin synthesis. 18.964 g of 4,4'-Methylenebis(phenyl isocyanate) 98% was charged to the reactor. The temperature was held at 40° C. for 40 minutes for solid softening. Next, 109.99 g of Poly(tetrahydrofuran) average M_n~2,900 was added and homogenized by stirring for 45 minutes at 40° C. To this homogenized mixture of 290 g of 1-Methyl-2-pyrrolidinone

anhydrous, 99.5% was added. The solution homogenized by mixing thoroughly for 40 minutes. Four drops Dibutyltin dilaurate 95% were added drop wise and the reaction mixture was held at 40° C. for one hour. After one hour 5.5051 grams glycidol were added and the temperature was held overnight until reaction completion.

Example 3 (E-3)	grams	eg. Wt	moles
4,4'-Methylenebis(phenyl isocyanate)	19.694	125	0.157552
Poly(tetrahydrofuran) average M_n ~2,900	109.99	1450	0.075855
glycidol	5.5051	74	0.074393
			0.150248

Example 4

This example describes the preparation of an inventive water loving coating (WLC) glycidyl carbamate dispersion (E-4). A 500 mL four neck reaction kettle with condenser, nitrogen inlet and model Gemini J-KEM temperature controller, mechanical stirrer, and heating mantel was used for resin synthesis. 18.964 g of 4,4'-Methylenebis(phenyl isocyanate) 98% was charged to the reactor. The temperature was held at 40° C. for 40 minutes for solid softening. Next, 19.464 g of Poly[di(ethylene glycol)adipate] average M_n~2500, 47.23 g of Poly(tetrahydrofuran) average M_n~2,900 was added, in the following order and homogenized by stirring for 45 minutes at 40° C. To this homogenized mixture 108.28 g of Poly (ethylene oxide) average M_v 100,000, powder was added immediately following the addition of 200 g of 1-Methyl-2-pyrrolidinone anhydrous, 99.5%. The solution homogenized by mixing thoroughly for 250 minutes. Four drops Dibutyltin dilaurate 95% were added drop wise and the reaction mixture was held at 40° C. for one hour. After one hour 4.048 grams glycidol were added and the temperature was held overnight until reaction completion

Example 4 (E-4)	grams	eg. Wt	moles
4,4'-Methylenebis(phenyl isocyanate)	18.964	125	0.151712
Poly [di(ethylene glycol) adipate] average M_n ~2,500	19.464	1250	0.015571
Poly(tetrahydrofuran) average M_n ~2,900	47.23	1450	0.032572
Poly (ethylene oxide) average M_v 100,000	108.28	50000	0.002166
glycidol	4.048	74	0.054703
			0.105012

Examples for Composition 2

Example 5

This example describes the preparation of an inventive water loving coating (WLC) glycidyl carbamate dispersion (E-5). A 500 mL four neck reaction kettle with condenser, nitrogen inlet and model Gemini J-KEM temperature controller, mechanical stirrer, and heating mantel was used for resin synthesis. 6.562 g of 4,4'-Methylenebis(phenyl isocyanate) 98% was charged to the reactor. The temperature was held at 40° C. for 40 minutes for solid softening. Next, 14.4 g of Poly[di(ethylene glycol)adipate] average M_n~2,500, 16.28 g of Poly(tetrahydrofuran) average M_n~2,900, and 0.6903 g of 2,2-Bis(hydroxymethyl) propionic acid 98% was added, in the following order and homogenized by stirring for 5 minutes at 40° C. To this homogenized mixture 50.0 of Poly (ethylene oxide) average M_v 100,000, powder was added immediately following the addition of 100 g of 1-Methyl-2-pyrrolidinone anhydrous, 99.5%. The solution homogenized by mixing thoroughly for 40 minutes. Four drops Dibutyltin dilaurate 95% were added drop wise and the reaction mixture was held at 40° C. for one hour. After one hour 0.3129 grams glycidol were added then 0.0741 grams of water were added after 45 minutes and the temperature was held overnight until reaction completion.

Example 5 (E-5)	grams	eg. Wt	moles
4,4'-Methylenebis(phenyl isocyanate)	6.562	125	0.052496
Poly [di(ethylene glycol) adipate] average M_n ~2500	14.4	1250	0.01152
Poly(tetrahydrofuran) average M_n ~2,900	16.28	1450	0.011228
2,2-Bis(hydroxymethyl)propionic acid	0.693	67.5	0.010267
Poly (ethylene oxide) average M_v 100,000	50	50000	0.001
glycidol	0.3129	74	0.004228
			0.038243

Example 6

This example describes the preparation of an inventive water loving coating (WLC) glycidyl carbamate dispersion (E-6). A 500 mL four neck reaction kettle with condenser, nitrogen inlet and model Gemini J-KEM temperature controller, mechanical stirrer, and heating mantel was used for resin synthesis. 10.33 g of 4,4'-Methylenebis(phenyl isocyanate) 98% was charged to the reactor. The temperature was held at 40° C. for 40 minutes for solid softening. Next, 25.82 g of Poly[di(ethylene glycol)adipate] average M_n~2,500, 29.95 g of Poly(tetrahydrofuran) average M_n~2,900, and 1.38 g of 2,2-Bis(hydroxymethyl) propionic acid 98% was added, in the following order and homogenized by stirring for 5 minutes at 40° C. To this homogenized mixture 30.98 g of Poly (ethylene oxide) average M_v 100,000, powder was added immediately following the addition of 1-Methyl-2-pyrrolidinone anhydrous, 99.5%. The solution homogenized by mixing thoroughly for 40 minutes. Four drops Dibutyltin dilaurate 95% were added drop wise and the reaction mixture was held at 40° C. for one hour. After one hour 1.52 grams glycidol were added and the temperature was held overnight until reaction completion.

Example 6 (E-6)	grams	eg. Wt	moles
4,4'-Methylenebis(phenyl isocyanate)	10.33	125	0.08264
Poly [di(ethylene glycol) adipate] average M_n ~2500	25.82	1250	0.020656
Poly(tetrahydrofuran) average M_n ~2,900	29.95	1450	0.020655
2,2-Bis(hydroxymethyl)propionic acid	1.38	67.5	0.020444
Poly (ethylene oxide) average M_v 100,000	30.98	50000	0.00062
glycidol	1.52	74	0.020541
			0.082916

Example 7

This example describes the preparation of an inventive water loving coating (WLC) glycidyl carbamate dispersion (E-7). A 500 mL four neck reaction kettle with condenser, nitrogen inlet and model Gemini J-KEM temperature controller, mechanical stirrer, and heating mantel was used for resin synthesis. 16.8 g of 1,6-Diisocyanatohexane>99.0% was charged to the reactor. The temperature was held at 40° C. for 40 minutes for solid softening. Next, 62.5 g of Poly[di(ethylene glycol)adipate] average M_n~2,500, 72.5 g of Poly(tet-

rahydrofuran) average M_n~2,900, and 3.35 g of 2,2-Bis(hydroxymethyl)propionic acid 98% was added, in the following order and homogenized by stirring for 5 minutes at 40° C. To this homogenized mixture 1-Methyl-2-pyrrolidinone anhydrous, 99.5% was added. The solution homogenized by mixing thoroughly for 40 minutes. Four drops Dibutyltin dilaurate 95% were added drop wise and the reaction mixture was held at 40° C. for one hour. After one hour 3.7 grams glycidol were added and the temperature was held overnight until reaction completion.

Example 7 (E-7)	grams	eg. Wt	moles
1,6-Diisocyanatohexane	16.8	84	0.2
Poly [di(ethylene glycol) adipate] average M_n ~2,500	62.5	1250	0.05
Poly(tetrahydrofuran) average M_n ~2,900	72.5	1450	0.05
2,2-Bis(hydroxymethyl)propionic acid	3.35	67.5	0.04963
Poly (ethylene oxide) average M_v 100,000	72.5	50000	0.00145
glycidol	3.7	74	0.05
			0.20108

Examples for Composition 3

Example 8

This example describes the preparation of an inventive water loving coating (WLC) glycidyl carbamate dispersion (E-8). A 500 mL four neck reaction kettle with condenser, nitrogen inlet and model Gemini J-KEM temperature controller, mechanical stirrer, and heating mantel was used for resin synthesis. 20.14 g of 4,4'-Methylenebis(cyclohexyl isocyanate), mixture of isomers 90% was charged to the reactor. The temperature was held at 40 degree C. for 40 minutes for solid softening. Next, 62.16 g of Poly(tetrahydrofuran) average M_n~2,900, and 3.061 g of 2,2-Bis(hydroxymethyl)propionic acid 98% was added, in the following order and homogenized by stirring for 5 minutes at 40° C. To this homogenized mixture 43.34 g of Poly(ethylene oxide) average M_v 100,000, powder was added immediately following the addition of 300 g of 1-Methyl-2-pyrrolidinone anhydrous, 99.5%. The solution homogenized by mixing thoroughly for 40 minutes. Six drops Dibutyltin dilaurate 95% were added drop wise and the reaction mixture was held at 40° C. for one hour. After one hour 3.2192 g of Adipic acid dihydrazide≥98% were added and mixed for two hours. To this homogenized mixture 7.5 grams glycidol were added and the temperature was held overnight until reaction completion.

Example 8 (E-8)	Grams	eg. Wt	moles
of 4,4'-Methylenebis(cyclohexyl isocyanate)	20.14	131	0.153740458
Poly(tetrahydrofuran) average M_n ~2,900	43.34	1450	0.029889655
2,2-Bis(hydroxy-methyl)propionic acid	3.061	67.5	0.045348148
Poly (ethylene oxide) average M_v 100,000	62.16	50000	0.0012432
Adipic acid dihydrazide	3.2192	87.1	0.036959816
glycidol	7.5	74	0.101351351
			0.214792171

Example 9

This example describes the preparation of an inventive water loving coating (WLC) glycidyl carbamate dispersion (E-9). A 500 mL four neck reaction kettle with condenser, nitrogen inlet and model Gemini J-KEM temperature controller, mechanical stirrer, and heating mantel was used for resin synthesis. 18.964 g of 4,4'-Methylenebis(phenyl isocyanate) 98% was charged to the reactor. The temperature was held at 40° C. for 40 minutes for solid softening. Next, 134.85 g of Poly(tetrahydrofuran) average M_n~2,900, was added and homogenized by stirring for 40 minutes at 40° C. To this homogenized mixture 216.75 g of Poly(ethylene oxide) average M_v 100,000, powder was added immediately following the addition of 290 g of 1-Methyl-2-pyrrolidinone anhydrous, 99.5%. The solution homogenized by mixing thoroughly for 40 minutes. Four drops Dibutyltin dilaurate 95% were added drop wise and the reaction mixture was held at 40° C. for one hour. After one hour 1.956 g of Adipic acid dihydrazide≥98% were added and mixed for two hours. To this homogenized mixture 0.33 grams glycidol were added and the temperature was held overnight until reaction completion.

Example 9 (E-9)	grams	eg. Wt	moles
4,4'-Methylenebis(phenyl isocyanate)	134.85	125	1.0788
Poly (ethylene oxide) average M_v 100,000	216.75	50000	0.004335
Adipic acid dihydrazide	1.956	87.1	0.0225028
glycidol	0.33	74	0.004459
Poly(tetrahydrofuran) average M_n ~2,900	134.85	1450	0.093
			0.1242968

Example 10

This example describes the preparation of an inventive water loving coating (WLC) glycidyl carbamate dispersion (E-10). A 500 mL four neck reaction kettle with condenser, nitrogen inlet and model Gemini J-KEM temperature controller, mechanical stirrer, and heating mantel was used for resin synthesis. 18.964 g of 4,4'-Methylenebis(phenyl isocyanate) 98% was charged to the reactor. The temperature was held at 40° C. for 40 minutes for solid softening. Next, 33.379 g of Poly[di(ethylene glycol)adipate] average M_n~2,500, 47.255 g of Poly(tetrahydrofuran) average M_n~2,900, and 2.000 g of 2,2-Bis(hydroxymethyl)propionic acid 98% was added, in the following order and homogenized by stirring for 5 minutes at 40° C. To this homogenized mixture 216.748 g of Poly(ethylene oxide) average M_v 100,000, powder was added immediately following the addition of 1-Methyl-2-pyrrolidinone anhydrous, 99.5%. The solution homogenized by mixing thoroughly for 40 minutes. Four drops Dibutyltin dilaurate 95% were added drop wise and the reaction mixture was held at 40° C. for one hour. After one hour 1.956 g of Adipic acid dihydrazide≥98% were added and mixed for two hours. To this homogenized mixture 0.33 grams glycidol were added and the temperature was held overnight until reaction completion

Example 10 (E-10)	grams	eg. Wt	moles
4,4'-Methylenebis(phenyl isocyanate)	18.964	125	0.151712
Poly [di(ethylene glycol) adipate] average M_n 2500	33.379	1250	0.0267032

-continued

Example 10 (E-10)	grams	eg. Wt	moles
Poly(tetrahydrofuran) average M_n ~2,900,	47.255	1450	0.03258
2,2-Bis(hydroxymethyl)propionic acid	2.000g	67.5	0.029629
Poly (ethylene oxide) average M_v 100,000	216.748	50000	0.04335
Adipic acid dihydrazide	1.956	87.1	0.02245569
glycidol	0.33	74	0.00445
			0.15916789

Example 11

This example describes the preparation of an inventive water loving coating (WLC) glycidyl carbamate dispersion (E-11). A 500 mL four neck reaction kettle with condenser, nitrogen inlet and model Gemini J-KEM temperature controller, mechanical stirrer, and heating mantel was used for resin synthesis. 18.972 g of 4,4'-Methylenebis(phenyl isocyanate) 98% was charged to the reactor. The temperature was held at 40° C. for 40 minutes for solid softening. Next, 33.29 g of Poly[di(ethylene glycol)adipate] average M_n~2,500, 47.92 g of Poly(tetrahydro-furan) average M_n~2,900, and 1.994 g of 2,2-Bis(hydroxymethyl)propionic acid 98% was added, in the following order and homogenized by stirring for 5 minutes at 40° C. To this homogenized mixture 43.349 g of Poly(ethylene oxide) average M_v 100,000, powder was added immediately following the addition of 290 g of 1-Methyl-2-pyrrolidinone anhydrous, 99.5%. The solution homogenized by mixing thoroughly for 40 minutes. Four drops Dibutyltin dilaurate 95% were added drop wise and the reaction mixture was held at 40° C. for one hour. After one hour 1.958 g of Adipic acid dihydrazide≥98% were added and mixed for two hours. To this homogenized mixture 2.426 grams glycidol were added and the temperature was held overnight until reaction completion.

Example 11 (E-11)	grams	eg. Wt	moles
4,4'-Methylenebis(phenyl isocyanate)	18.792	125	0.150336
Poly [di(ethylene glycol) adipate] average M_n ~2,500	33.29	1250	0.026632
Poly(tetrahydrofuran) average M_n ~2,900	47.92	1450	0.03304828
2,2-Bis(hydroxymethyl)propionic acid	1.994	67.5	0.02954074
Poly (ethylene oxide) average M_v 100,000	43.349	50000	0.00086698
Adipic acid dihydrazide	1.958	87.1	0.02247991
glycidol	2.426	74	0.03278378
			0.14535169

Examples for Composition 4

Example 12

This example describes the preparation of an inventive water loving coating (WLC) glycidyl carbamate dispersion (E-12). A 500 mL four neck reaction kettle with condenser, nitrogen inlet and model Gemini J-KEM temperature controller, mechanical stirrer, and heating mantel was used for resin synthesis. 18.964 g of 4,4'-Methylenebis(phenyl isocyanate) 98% was charged to the reactor. The temperature was held at 40° C. for 40 minutes for solid softening. Next, 40.456 g of Poly[di(ethylene glycol)adipate] average M_n~2,500, 45.911 g of Poly(tetrahydrofuran) average M_n~2,900, and 1.939 g of 2,2-Bis(hydroxymethyl)propionic acid 98% was added, in the following order and homogenized by stirring for 5 minutes at 40° C. To this homogenized mixture 210.0 g of Poly (ethylene oxide) average M_v 100,000, powder was added immediately following the addition of 290 g of 1-Methyl-2-pyrrolidinone anhydrous, 99.5%. The solution homogenized by mixing thoroughly for 250 minutes. Four drops Dibutyltin dilaurate 95% were added drop wise and the reaction mixture was held at 40° C. for one hour. After one hour 1.37 g of Adipic acid dihydrazide≥98% were added and mixed for two hours. To this homogenized mixture 1.436 grams glycidol were added and the temperature was held overnight until reaction completion. The final addition involved 0.3533 grams water to form a urea.

Example 12 (E-12)	grams	eg. Wt	moles
4,4'-Methylenebis(phenyl isocyanate)	18.964	125	0.151712
Poly [di(ethylene glycol) adipate] average M_n ~2,500	40.456	1250	0.0323648
Poly(tetrahydrofuran) average M_n ~2,900	45.911	1450	0.031662759
2,2-Bis(hydroxymethyl)propionic acid	1.939	67.5	0.028725926
Poly (ethylene oxide) average M_v 100,000	210	50000	0.0042
Adipic acid dihydrazide	1.37	87.1	0.015729047
glycidol	1.436	74	0.019405405
			0.132087937
WATER	0.3533	18	0.01963

Example 13

This example describes the preparation of an inventive water loving coating (WLC) glycidyl carbamate dispersion (E-13). A 500 mL four neck reaction kettle with condenser, nitrogen inlet and model Gemini J-KEM temperature controller, mechanical stirrer, and heating mantel was used for resin synthesis. 18.964 g of 4,4'-Methylenebis(phenyl isocyanate) 98% was charged to the reactor. The temperature was held at 40° C. for 40 minutes for solid softening. Next, 33.38 g of Poly[di(ethylene glycol)adipate] average M_n~2500, 47.23 g of Poly(tetrahydrofuran) average M_n~2,900 was added, and 1.99 g of 2,2-Bis(hydroxymethyl)propionic acid 98% was added, in the following order and homogenized by stirring for 45 minutes at 40° C. To this homogenized mixture 53.57 g of Poly(ethylene oxide) average M_v 100,000, powder was added immediately following the addition of 200 g of 1-Methyl-2-pyrrolidinone anhydrous, 99.5%. The solution homogenized by mixing thoroughly for 250 minutes. Four drops Dibutyltin dilaurate 95% were added drop wise and the reaction mixture was held at 40° C. for one hour. After one hour 1.354 g of Adipic acid dihydrazide≥98% were added and mixed for two hours. To this homogenized mixture 2.427 grams glycidol were added and the temperature was held overnight until reaction completion. The final addition involved 0.2409 grams water to form a urea.

Example 13 (E-13)	grams	eg. Wt	moles
4,4'-Methylenebis(phenyl isocyanate)	18.964	125	0.151712
Poly [di(ethylene glycol) adipate] average M_n ~2,500	33.38	1250	0.026704
Poly(tetrahydrofuran) average M_n ~2,900	47.25	1450	0.032586207

-continued

Example 13 (E-13)	grams	eg. Wt	moles
2,2-Bis(hydroxymethyl)propionic acid	1.9999	67.5	0.029628148
Poly (ethylene oxide) average M_v 100,000	53.57	50000	0.0010714
Adipic acid dihydrazide	1.354	87.1	0.01554535
glycidol	2.427	74	0.032797297
			0.138332403
WATER	0.2409	18	0.013382

Examples for Composition 5

Example 14

This example describes the preparation of an inventive water-loving coating (WLC) glycidyl carbamate dispersion (E-14). A 500 mL four neck reaction kettle with condenser, nitrogen inlet and model Gemini J-KEM temperature controller, mechanical stirrer, and heating mantel was used for resin synthesis. 18.964 g of 4,4'-Methylenebis(phenyl isocyanate) 98% was charged to the reactor. The temperature was held at 40° C. for 40 minutes for solid softening. Next, 40.457 g of Poly[di(ethylene glycol)adipate] average M_n~2,500, 45.911 g of Poly(tetrahydrofuran) average M_n~2,900, and 1.939 g of 2,2-Bis(hydroxymethyl)propionic acid 98% was added, in the following order and homogenized by stirring for 5 minutes at 40° C. To this homogenized mixture 210.71 g of Poly(ethylene oxide) average M_v 100,000, powder was added immediately following the addition of 290 g of 1-Methyl-2-pyrrolidinone anhydrous, 99.5%. The solution homogenized by mixing thoroughly for 40 minutes. Four drops Dibutyltin dilaurate 95% were added drop wise and the reaction mixture was held at 40° C. for one hour. After one hour 1.3789 g of Adipic acid dihydrazide≥98% were added and mixed for two hours. To this homogenized mixture 1.436 grams glycidol were added and the temperature was held overnight until reaction completion.

Example 14 (E-14) POLYURETHANE UREA W/EXCESS NCO	grams	eg. Wt	moles
4,4'-Methylenebis(phenyl isocyanate)	18.964	125	0.151712
Poly [di(ethylene glycol) adipate] average M_n ~2,500	40.457	1250	0.0323656
Poly(tetrahydrofuran) average M_n ~2,900	45.911	1450	0.031662759
2,2-Bis(hydroxymethyl)propionic acid 98%	1.939	67.5	0.028725926
Adipic acid dihydrazide	1.3789	87.1	0.015831228
glycidol	1.436	74	0.019405405
			0.127990918

Examples for the Cross-Linking Reaction

Example 15

This example describes the preparation of an inventive water loving coating (WLC) glycidyl carbamate dispersion (E-15). A 500 mL four neck reaction kettle with condenser, nitrogen inlet and model Gemini J-KEM temperature controller, mechanical stirrer, and heating mantel was used for resin synthesis. 10.33 g of 4,4'-Methylenebis(phenyl isocyanate) 98% was charged to the reactor. The temperature was held at 40° C. for 40 minutes for solid softening. Next, 25.82 g of Poly[di(ethylene glycol)adipate] average M_n~2,500, 29.95 g of Poly(tetrahydrofuran) average M_n~2,900, and 1.38 g of 2,2-Bis(hydroxymethyl) propionic acid 98% was added, in the following order and homogenized by stirring for 5 minutes at 40° C. To this homogenized mixture 30.98 g of Poly (ethylene oxide) average M_v 100,000, powder was added immediately following the addition of 1-Methyl-2-pyrrolidinone anhydrous, 99.5%. The solution homogenized by mixing thoroughly for 40 minutes. Four drops Dibutyltin dilaurate 95% were added drop wise and the reaction mixture was held at 60° C. for one hour for homopolymerization. After one hour 1.52 grams glycidol were added and the temperature was held for 72 hours.

Example 15 (E-15)	grams	eg. Wt	moles
4,4'-Methylenebis(phenyl isocyanate)	8.264	125	.066112
Poly [di(ethylene glycol) adipate] average M_n ~2500	20.656	1250	.0165248
Poly(tetrahydrofuran) average M_n ~2,900	23.96	1450	.016524
2,2-Bis(hydroxymethyl)propionic acid	1.104	67.5	.0163552
Poly (ethylene oxide) average M_v 100,000	24.78	50000	.000496
glycidol	1.21	74	.016432
			.0663328

Example 16

This example describes the preparation of an inventive water-loving coating (WLC) Epoxy urethane alkylene oxide reactive coating compositions. A 500 mL four neck reaction kettle with condenser, nitrogen inlet and model Gemini J-KEM temperature controller, mechanical stirrer, and heating mantel was used for resin synthesis. 18.964 g of 4,4'-Methylenebis(phenyl isocyanate) 98% was charged to the reactor. The temperature was held at 40 degree C. for 40 minutes for solid softening. Next, 109.99 g of Poly(tetrahydrofuran) average M_n~2,900 was added and homogenized by stirring for 45 minutes at 40.degree. C. To this homogenized mixture of 290 g of 1-Methyl-2-pyrrolidinone anhydrous, 99.5% was added. The solution homogenized by mixing thoroughly for 40 minutes. Four drops Dibutyltin dilaurate 95% were added drop wise and the reaction mixture was held at 40 degrees C. for one hour. After one hour 5.5051 grams glycidol were added and the temperature was held overnight until reaction completion.

Example 17

This example describes the preparation of an inventive water-loving coating (WLC) Epoxy urethane ester carboxylic acid alkylene oxide reactive coating compositions. A 500 mL four neck reaction kettle with condenser, nitrogen inlet and model Gemini J-KEM temperature controller, mechanical stirrer, and heating mantel was used for resin synthesis. 16.8 g of 1,6-Diisocyanatohexane>99.0% was charged to the reactor. The temperature was held at 40° C. for 40 minutes for solid softening. Next, 62.5 g of Poly[di(ethylene glycol)adipate] average M_n~2,500, 72.5 g of Poly(tetrahydrofuran) average M_n~2,900, and 3.35 g of 2,2-Bis(hydroxymethyl) propionic acid 98% was added, in the following order and homogenized by stirring for 5 minutes at 40° C. To this homogenized mixture 150 grams of Poly(ethylene oxide) average M_v 100,000, powder was added immediately following the addition of 1-Methyl-2-pyrrolidinone anhydrous, 99.5%. The solution homogenized by mixing thoroughly for 40 minutes. Four drops Dibutyltin dilaurate 95% were added

drop wise and the reaction mixture was held at ° C. for one hour. After one hour 3.7 grams glycidol were added and the temperature was held overnight until reaction completion.

Example 18

This example describes the preparation of an inventive water-loving coating (WLC) Epoxy urethane urea carboxylic acid alkylene oxide reactive coating compositions. A 500 mL four neck reaction kettle with condenser, nitrogen inlet and model Gemini J-KEM temperature controller, mechanical stirrer, and heating mantel was used for resin synthesis. 18.964 g of 4,4'-Methylenebis(phenyl isocyanate) 98% was charged to the reactor. The temperature was held at 40° C. for 40 minutes for solid softening. Next, 33.379 g of Poly[di (ethylene glycol)adipate] average M_n~2,500, 47.255 g of Poly(tetrahydrofuran) average M_n~2,900, and 2.000 g of 2,2-Bis(hydroxymethyl)propionic acid 98% was added, in the following order and homogenized by stirring for 5 minutes at 40° C. To this homogenized mixture 216.748 g of Poly(ethylene oxide) average 100,000, powder was added immediately following the addition of 1-Methyl-2-pyrrolidinone anhydrous, 99.5%. The solution homogenized by mixing thoroughly for 40 minutes. Four drops Dibutyltin dilaurate 95% were added drop wise and the reaction mixture was held at 40 degrees C. for one hour. After one hour 1.956 g of Adipic acid dihydrazide≥98% were added and mixed for two hours. To this homogenized mixture 0.33 grams glycidol were added and the temperature was held overnight until reaction completion.

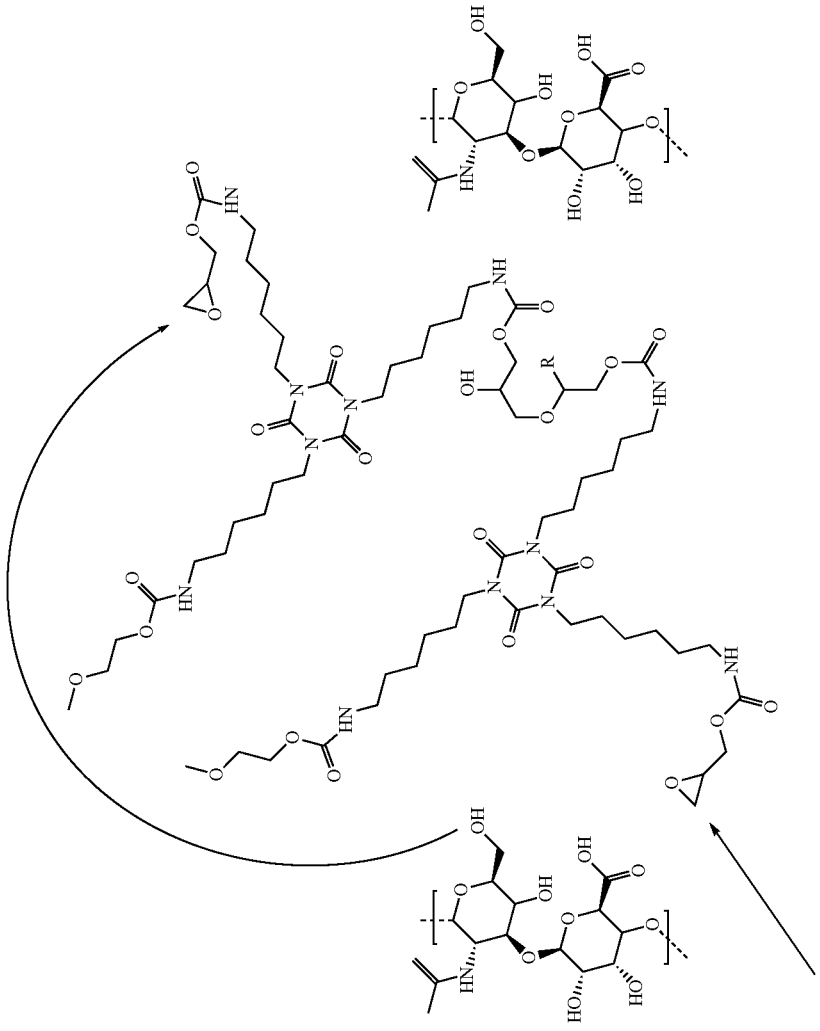
Example 19

This example describes the preparation of an inventive water loving coating (WLC) Epoxy urethane urea carboxylic acid alkylene oxide reactive coating compositions. A 500 mL four neck reaction kettle with condenser, nitrogen inlet and model Gemini J-KEM temperature controller, mechanical stirrer, and heating mantel was used for resin synthesis. 18.964 g of 4,4'-Methylenebis(phenyl isocyanate) 98% was charged to the reactor. The temperature was held at 40° C. for 40 minutes for solid softening. Next, 40.456 g of Poly[di (ethylene glycol)adipate] average M_n~2,500, 45.911 g of Poly(tetrahydrofuran) average M_n~2,900, and 1.939 g of 2,2-Bis(hydroxymethyl)propionic acid 98% was added, in the following order and homogenized by stirring for 5 minutes at 40° C. To this homogenized mixture 210.0 g of Poly(ethylene oxide) average M_v 100,000, powder was added immediately following the addition of 290 g of 1-Methyl-2-pyrrolidinone anhydrous, 99.5%. The solution homogenized by mixing thoroughly for 250 minutes. Four drops Dibutyltin dilaurate 95% were added drop wise and the reaction mixture was held at 40 degrees C. for one hour. After one hour 1.37 g of Adipic acid dihydrazide≥98% were added and mixed for two hours. To this homogenized mixture 1.436 grams glycidol were added and the temperature was held overnight until reaction completion. The final addition involved 0.3533 grams water to form a urea.

SUMMARY OF WLC CONNECTIVITY

Basecoat terminal epoxy groups react with top coat epoxy groups through ARM amine functionality which increase adhesive strength. Basecoat chemistry contains Easaqua XM-502, which is added during the base coat mixing step. This aqueous isocyanate contains mpeg for use in water based applications. When this material is added to basecoat the isocyanate reacts with the carboxylic acid and open epoxide hydroxyl groups for basecoat cohesive strength. Easaqua XM-502 also reacts with top coat ARM and open hydroxyl groups for adhesive strength.

Once crosslinked, with Easaqua XM-502, then the base coat becomes a hydrogel. The hydrogel crosslinks take in water and swell via soft segments (Terethane, PEO and PEDGA) to render the coating water loving with high lubricity. Crosslink chemistry allows water to become retained within the walls of the soft segment without going into solution. This chemical and physical process leads to an extremely durable and lubricious coating.



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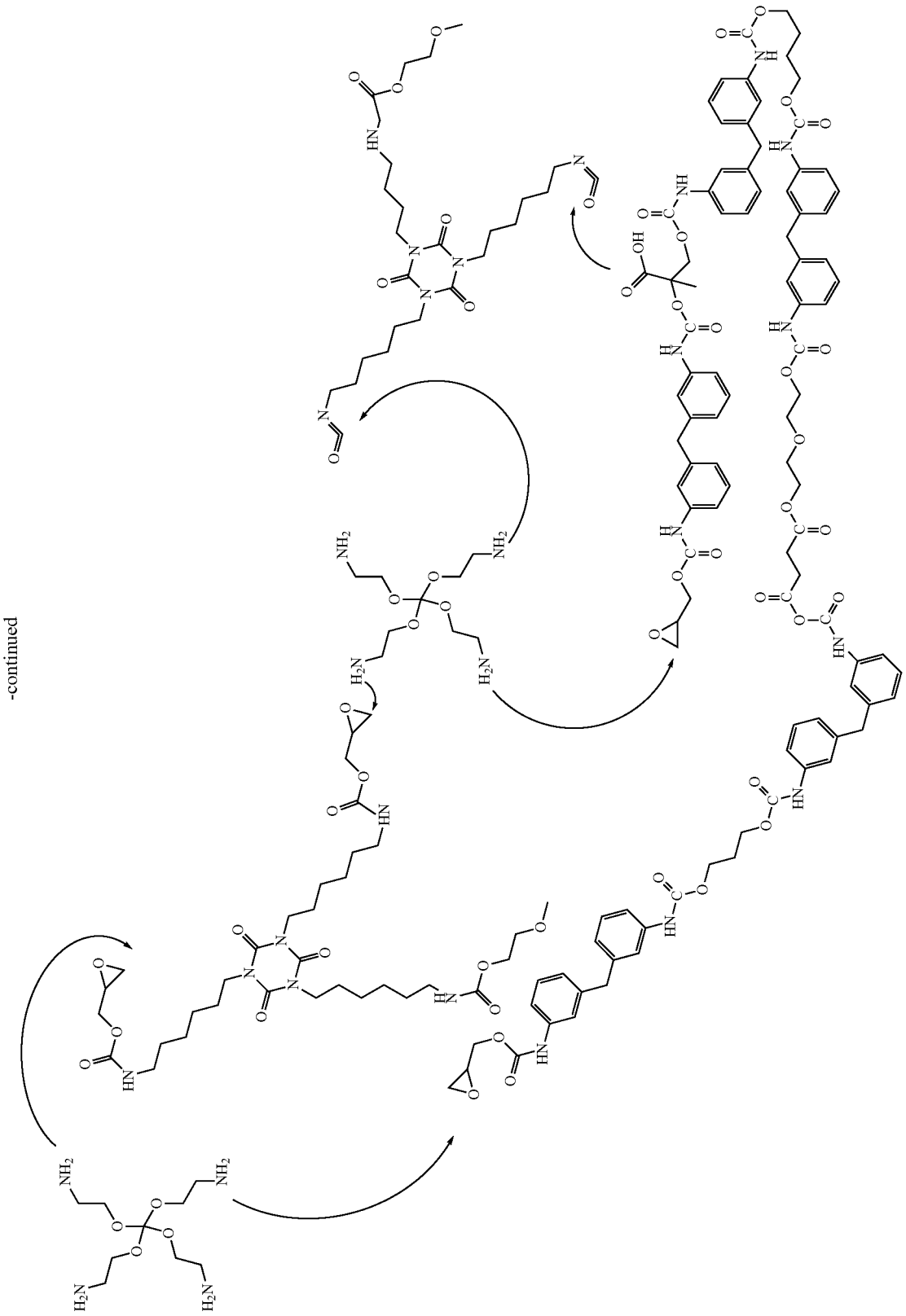


WLC Oxirane Connections

A resin sample of an aqueous polyurethane polymer was submitted to NSL Analytical Laboratories on Nov. 2, 2009 for characterization of the polymer. Various Mass Spectrometry techniques were utilized in this characterization, including Electro-Spray Ionization (ESI), Matrix Assisted Laser Desorption Ionization (MALDI) and Chemical Ionization (CI). The following are abbreviations are used to describe findings:

GA	glycidol alcohol
DEG	diethylene glycol
DMPA	dimethylolpropionic acid
DEGA	diethyleneglycol adipate
MDI	methylene-diiscocyanate
PEG	polyethylene glycol
PDEGA	polydiethyleneglycol adipate

Abbreviations Used to Describe Findings

The sample was analyzed by 1H NMR with the sample dissolved in TCE. This was able to provide the monomer ratios listed below.

MDI	1 mol
Adipic	2.875 mol
DEG	3.075 mol
PTMEG (poly THF)	11 mol of THF
PEG (i.e. PEO)	24 moles of EO
Glycidolcarbonate	0.5 mol
DMPA	0.27 mol

Monomer Ratios Determined by Proton NMR

Coating Example Composition 1

Materials as synthesized above were then applied to substrates noted below in the following fashion:

Coating Polyurethane Tungsten Loaded Jacket

a. An aqueous and or solvent dispersion basecoat was prepared from 8.8 g of composition 1 AND 0.2 Easaqua XM-502 were then added to the formulation and stirred at 900 rpm for 15 minutes.

b. Basecoat (of this invention) was applied to the polyurethane jacketed wire, by dip coating, at a set speed for a desired film thickness

c. The basecoat was then cured either at ambient or thermally until no longer-tacky

d. An aqueous dispersion topcoat was prepared with crosslinker in the following order: (1) 0.005 grams Poly (ethylene oxide), 4-arm, amine terminated average M_n~10,000 was added to a one ounce bottle then (2) 0.02 '956 patent. To this crosslinker 11.576 grams of modified hyaluronan top coat formulated resin was added and crosslinker was stirred at 1800 rpm for 5 minutes

e. Topcoat of the concurrently filed application noted above was then applied at a set speed for desired film thickness

f. The coating was then cured at ambient or thermally until fully cured

g. The final cured product resulted in a highly lubricious coating

Coating Metal Wire Substrate with Adhesion Promoter

Preparation of Adhesion Promoter

i. 100 mL ETOH (ETOH anhydrous) provided by Sigma

ii. Add 5.0 gram water

iii. Stir 10 minutes

iv. Add 3.84 grams 3-aminopropyltriethoxysilane (Provided by Gelest)

v. Mix 5 minutes

a. Coating wire with adhesion promoter

vi. Pour adhesion promoter into 100 mL burette (use shaker to mix)

vii. Place wire in graduated cylinder solution for 10 minutes

viii. Take wire out of solution and place in 125 C oven for 10 minutes

Polyurethane tungsten loaded jacket

b. An aqueous and or solvent dispersion basecoat was prepared from 8.8 g of composition 1 AND 0.015 Easaqua XM-502 were then added to the formulation and stirred at 900 rpm for 15 minutes.

c. The wire from step a-viii was taken out of the 125 C oven for coating

d. Basecoat was applied to the metal wire substrate with adhesion promoter, by dip coating, at a set speed for a desired film thickness

e. The basecoat was then cured either at ambient or thermally until no longer-tacky

f. An aqueous dispersion intermediate layer was prepared with Easaqua XM-502 (0.015) crosslinker, '956 patent and adipic acid dihydrazide (0.02). To this crosslinker 8.8 grams composition 1 plus water were formulated and stirred at 1800 RPM for 5 minutes. The intermediate layer contained 0.01 TPP catalyst.

g. Intermediate layer was then applied at a set speed for desired film thickness

h. The intermediate layer was then cured either at ambient or thermally until no longer-tacky

i. An aqueous dispersion topcoat was prepared with crosslinker in the following order: (1) 0.01 grams adipic acid dihydrazide was added to a one ounce bottle then (2) 0.01 grams PZ-28 To this crosslinker 11.576 grams composition 2 was added to the crosslinker, which was stirred at 1800 rpm for 5 minutes

j. Topcoat was then applied at a set speed for desired film thickness

k. The coating was then cured at ambient or thermally until fully cured

l. The final cured product resulted in a highly lubricious coating

Coating Example Composition 3

Materials were then applied to substrates noted below in the following fashion:

Coating Polyurethane Tungsten Loaded Jacket

h. An aqueous and or solvent dispersion basecoat was prepared from 8.8 g of composition 3 AND 0.2 Polyaziridine PZ-28 were then added to the formulation and stirred at 900 rpm for 15 minutes.

i. Basecoat was applied to the polyurethane jacketed wire, by dip coating, at a set speed for a desired film thickness

j. The basecoat was then cured either at ambient or thermally until no longer-tacky

k. An aqueous dispersion topcoat was prepared with crosslinker in the following order: (1) 0.002 grams Poly (ethylene oxide), 4-arm, amine terminated average M_n~10,000 was added to a one ounce bottle then (2) 0.0252 grams '956 patent. To this crosslinker 11.576 grams of modified hyaluronan top coat formulated resin was added and crosslinker was stirred at 1800 rpm for 5 minutes

l. Topcoat was then applied at a set speed for desired film thickness

m. The coating was then cured at ambient or thermally until fully cured

n. The final cured product resulted in a highly lubricious coating

Coating Metal Wire Substrate with Adhesion Promoter

Preparation of Adhesion Promoter

i. 100 mL ETOH (ETOH anhydrous) provided by Sigma

ii. Add 5.0 gram water

iii. Stir 10 minutes

1. Add 3.84 grams 3-aminoethyltriethoxysilane (Provided by Gelest)
iv.
v. Mix 5 minutes
m. Coating wire with adhesion promoter
vi. Pour adhesion promoter into 100 mL burette (use shaker to mix)
vii. Place wire in graduated cylinder solution for 10 minutes
viii. Take wire out of solution and place in 125 C oven for 10 minutes

Polyurethane tungsten loaded jacket

n. An aqueous and or solvent dispersion basecoat was prepared from 8.8 g of composition 3 AND 0.2 Polyaziridine PZ-28 were then added to the formulation and stirred at 900 rpm for 15 minutes.
o. The wire from step viii was taken out of the 125 C oven for coating
p. Basecoat was applied to the metal wire substrate with adhesion promoter, by dip coating, at a set speed for a desired film thickness
q. The basecoat was then cured either at ambient or thermally until no longer-tacky
r. An aqueous dispersion topcoat was prepared with crosslinker in the following order: (1) 0.002 grams Poly (ethylene oxide), 4-arm, amine terminated average M_n~10,000 was added to a one ounce bottle then (2) 0.0252 grams '956 patent. To this crosslinker 11.576 grams of modified hyaluronan top coat formulated resin was added and crosslinker was stirred at 1800 rpm for 5 minutes
s. Topcoat was then applied at a set speed for desired film thickness
t. The coating was then cured at ambient or thermally until fully cured
u. The final cured product resulted in a highly lubricious coating

Coating Example Composition 5

Materials were then applied to substrates noted below in the following fashion:

Coating Polyurethane Tungsten Loaded Jacket

o. An aqueous and or solvent dispersion basecoat was prepared from 8.8 g of composition 5 and stirred at 900 rpm for 15 minutes.
p. Basecoat was applied to the polyurethane jacketed wire, by dip coating, at a set speed for a desired film thickness
q. The basecoat was then cured either at ambient or thermally until no longer-tacky
r. An aqueous dispersion topcoat was prepared with crosslinker in the following order: (1) 0.0005 grams Poly(ethylene oxide), 4-arm, amine terminated average M_n~10,000 was added to a one ounce bottle then (2) 0.0000271 grams '956 patent. To this crosslinker 11.576 grams of modified hyaluronan top coat formulated resin was added and crosslinker was stirred at 1800 rpm for 5 minutes
s. Topcoat was then applied at a set speed for desired film thickness
t. The coating was then cured at ambient or thermally until fully cured
u. The final cured product resulted in a highly lubricious coating

Coating Metal Wire Substrate with Adhesion Promoter

Preparation of Adhesion Promoter

i. 100 mL ETOH (ETOH anhydrous) provided by Sigma
ii. Add 5.0 gram water
iii. Stir 10 minutes
iv. Add 3.84 grams 3-aminopropyltriethoxysilane (Provided by Gelest)
v. Mix 5 minutes
v. Coating wire with adhesion promoter
vi. Pour adhesion promoter into 100 mL burette (use shaker to mix)
vii. Place wire in graduated cylinder solution for 10 minutes
viii. Take wire out of solution and place in 125 C oven for 10 minutes

Polyurethane tungsten loaded jacket

v. An aqueous and or solvent dispersion basecoat was prepared from 8.8 g of composition 5 and stirred at 900 rpm for 15 minutes.
w. Basecoat was applied to the polyurethane jacketed wire, by dip coating, at a set speed for a desired film thickness
x. The basecoat was then cured either at ambient or thermally until no longer-tacky
y. An aqueous dispersion topcoat was prepared with crosslinker in the following order: (1) 0.0005 grams Poly(ethylene oxide), 4-arm, amine terminated average M_n~10,000 was added to a one ounce bottle then (2) 0.0000271 grams '956 patent. To this crosslinker 11.576 grams of modified hyaluronan top coat formulated resin was added and crosslinker was stirred at 1800 rpm for 5 minutes
z. Topcoat was then applied at a set speed for desired film thickness
aa. The coating was then cured at ambient or thermally until fully cured
w. The final cured product resulted in a highly lubricious coating

Coating Example Composition 7

Materials were then applied to substrates noted below in the following fashion:

Coating Polyurethane Tungsten Loaded Jacket

bb. An aqueous and or solvent dispersion basecoat was prepared from 8.8 g of composition 7 AND 0.2 Easaqua XM-502 were then added to the formulation and stirred at 900 rpm for 15 minutes Basecoat was applied to the polyurethane jacketed wire, by dip coating, at a set speed for a desired film thickness
cc. The basecoat was then cured either at ambient or thermally until no longer-tacky
dd. An aqueous dispersion topcoat was prepared with crosslinker in the following order: (1) 0.02 grams Poly (ethylene oxide), 4-arm, amine terminated average M_n~10,000 was added to a one ounce bottle then (2) 0.015 grams '956 patent. To this crosslinker 11.576 grams of modified hyaluronan top coat formulated resin was added and crosslinker was stirred at 1800 rpm for 5 minutes
ee. Topcoat was then applied at a set speed for desired film thickness
ff. The coating was then cured at ambient or thermally until fully cured
gg. The final cured product resulted in a highly lubricious coating

Coating Metal Wire Substrate with Adhesion Promoter

Preparation of Adhesion Promoter

i. 100 mL ETOH (ETOH anhydrous) provided by Sigma
ii. Add 5.0 gram water
iii. Stir 10 minutes
iv. Add 3.84 grams 3-aminopropyltriethoxysilane
v. Mix 5 minutes
x. Coating wire with adhesion promoter
vi. Pour adhesion promoter into 100 mL burette (use shaker to mix)
vii. Place wire in graduated cylinder solution for 10 minutes
viii. Take wire out of solution and place in 125 C oven for 10 minutes

Polyurethane tungsten loaded jacket

hh. An aqueous and or solvent dispersion basecoat was prepared from 8.8 g of composition 7 AND 0.2 Easaqua XM-502 were then added to the formulation and stirred at 900 rpm for 15 minutes Basecoat was applied to the polyurethane jacketed wire, by dip coating, at a set speed for a desired film thickness

ii. The basecoat was then cured either at ambient or thermally until no longer-tacky

jj. An aqueous dispersion topcoat was prepared with crosslinker in the following order: (1) 0.005 grams Poly (ethylene oxide), 4-arm, amine terminated average M_n~10,000 was added to a one ounce bottle then (2) 0.01 grams '956 patent. To this crosslinker 11.576 grams of modified hyaluronan top coat formulated resin was added and crosslinker was stirred at 1800 rpm for 5 minutes

kk. Topcoat was then applied at a set speed for desired film thickness

ll. The coating was then cured at ambient or thermally until fully cured

y. The final cured product resulted in a highly lubricious and durable coating

Coating Example Composition 9

Materials were then applied to substrates noted below in the following fashion:

Coating Polyurethane Tungsten Loaded Jacket

mm. An aqueous and or solvent dispersion basecoat was prepared from 8.8 g of composition 9 AND 0.02 Easaqua XM-502 were then added to the formulation and stirred at 900 rpm for 15 minutes Basecoat was applied to the polyurethane jacketed wire, by dip coating, at a set speed for a desired film thickness

nn. The basecoat was then cured either at ambient or thermally until no longer-tacky

oo. An aqueous dispersion topcoat was prepared with crosslinker in the following order: (1) 0.002 grams Poly (ethylene oxide), 4-arm, amine terminated average M_n~10,000 was added to a one ounce bottle then (2) 0.002 grams '956 patent. To this crosslinker 11.576 grams of modified hyaluronan top coat formulated resin was added and crosslinker was stirred at 1800 rpm for 5 minutes

pp. Topcoat was then applied at a set speed for desired film thickness

qq. The coating was then cured at ambient or thermally until fully cured

rr. The final cured product resulted in a highly lubricious coating

Coating Metal Wire Substrate with Adhesion Promoter

Preparation of Adhesion Promoter

i. 100 mL ETOH (ETOH anhydrous) provided by Sigma

ii. Add 5.0 gram water

iii. Stir 10 minutes

2. Add 3.84 grams 3-trimethoxysilylpropyl-diethylenetriamine (Provided by Gelest)

iv.

v. Mix 5 minutes

z. Coating wire with adhesion promoter

vi. Pour adhesion promoter into 100 mL burette (use shaker to mix)

vii. Place wire in graduated cylinder solution for 10 minutes

viii. Take wire out of solution and place in 125 C oven for 10 minutes

Polyurethane tungsten loaded jacket

ss. An aqueous and or solvent dispersion basecoat was prepared from 8.8 g of composition 9 AND 0.02 Easaqua XM-502 were then added to the formulation and stirred at 900 rpm for 15 minutes Basecoat was applied to the polyurethane jacketed wire, by dip coating, at a set speed for a desired film thickness

tt. The basecoat was then cured either at ambient or thermally until no longer-tacky

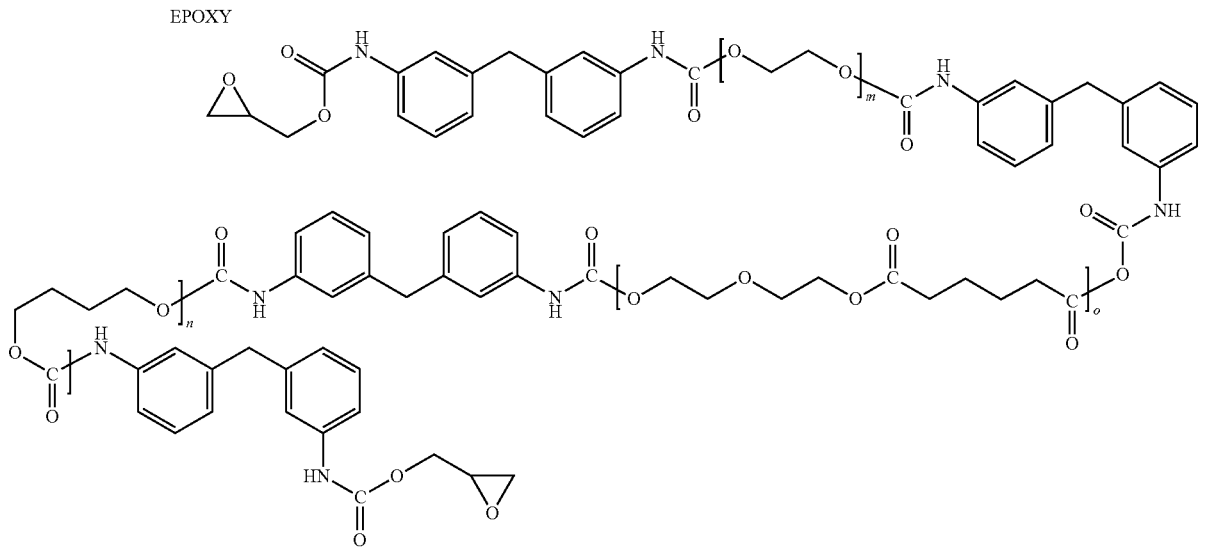
uu. An aqueous dispersion topcoat was prepared with crosslinker in the following order: (1) 0.002 grams Poly (ethylene oxide), 4-arm, amine terminated average M_n~10,000 was added to a one ounce bottle then (2) 0.002 grams '956 patent. To this crosslinker 11.576 grams of modified hyaluronan top coat formulated resin was added and crosslinker was stirred at 1800 rpm for 5 minutes

vv. Topcoat was then applied at a set speed for desired film thickness

ww. The coating was then cured at ambient or thermally until fully cured

xx. The final cured product resulted in a highly lubricious and durable coating

1. A composition comprising epoxy urethane alkylene oxide reactive coating compositions of the structure of formula (I).



2. The composition of paragraph 1, wherein the epoxy urethane alkylene oxide reactive coating compositions are

(a) Polytrimethylene ether glycol, with n having a number average molecular weight in the range of about 1,000 to about 4,000,000 where n=11 to about 46.

(b) Optional Polyethylene oxide, with m having a number average molecular weight in the range of about 18,000 to about 2,000,000 where n=375 to about 41,667

(c) Optional Poly[di(ethylene glycol)adipate, with o having a number average molecular weight in the range of about 400 to about 10,000.00 where n=2 to about 50

(d) Glycidyl moieties are represented by the addition of glycidol

3. A composition comprising epoxy urethane ester carboxylic acid alkylene oxide reactive coating compositions of the following structure (II):

(a) Poly[di(ethylene glycol) adipate having a number average molecular weight in the range of about 400 to about 10,000.00 where n=2 to about 50

(b) Optional Polytrimethylene ether glycol having a number average molecular weight in the range of about 1,000 to about 4,000,000 where n=11 to about 46.

(c) Optional Polyethylene oxide having a number average molecular weight in the range of about 18,000 to about 2,000,000 where n=375 to about 41,667

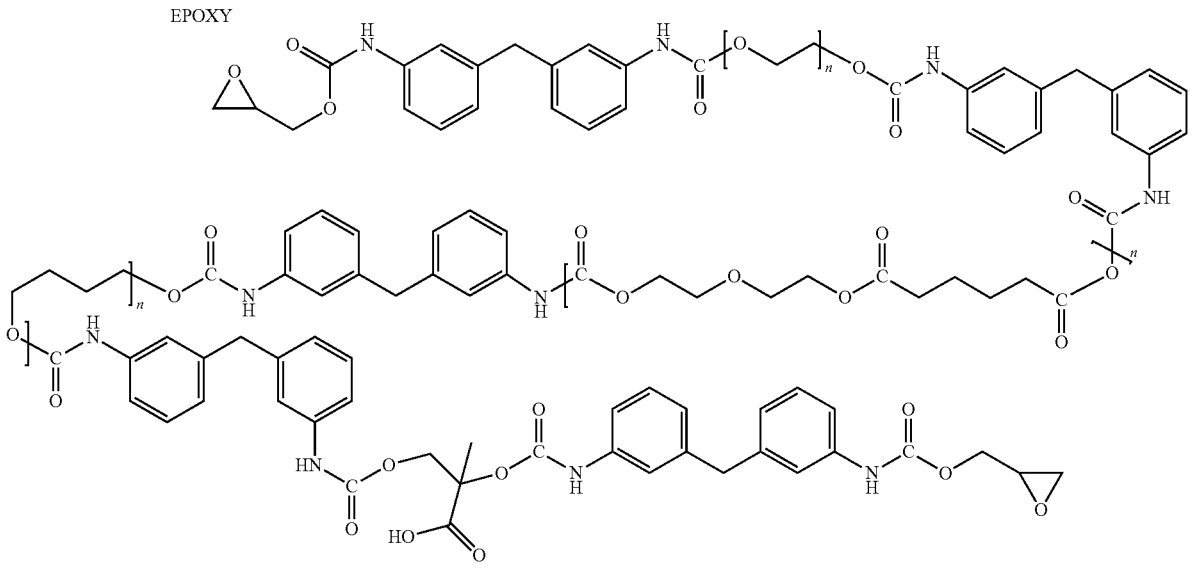
(d) Acid moieties are represented by the addition of dimethylol propionic acid

(e) Glycidyl moieties are represented by the addition of glycidol

(f) Excess isocyanate can react with dimethylol propionic acid to form an amide resulting in a urea

URETHANE

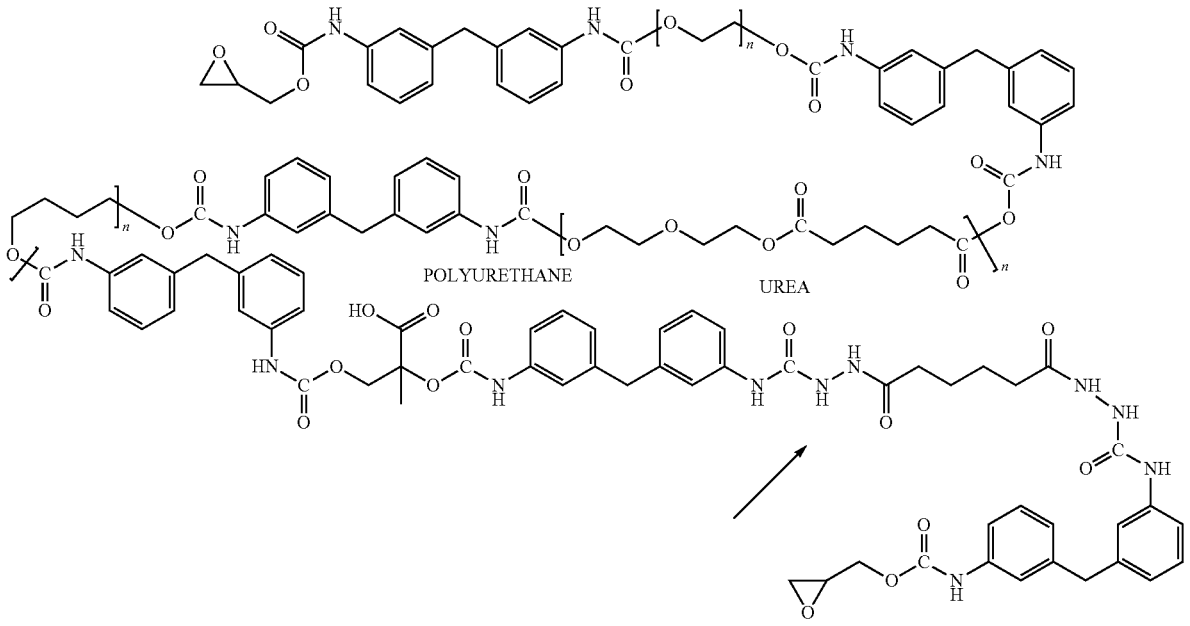
EPOXY



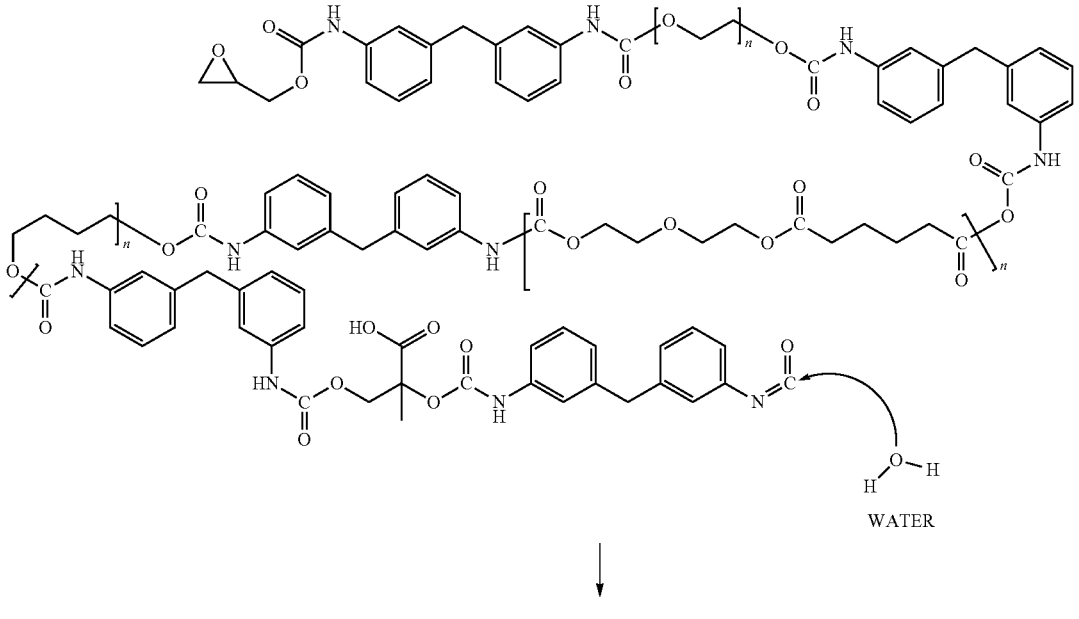
CARBOXYLIC ACID

4. The composition of paragraph 3, wherein the epoxy urethane ester carboxylic acid alkylene oxide reactive coating compositions are

5. A composition comprising epoxy urethane urea carboxylic acid alkylene oxide reactive coating compositions of the following structure (III):



6. The composition of paragraph 5, wherein the epoxy urethane urea carboxylic acid alkylene oxide reactive coating compositions are:
   (a) Poly[di(ethylene glycol) adipate having a number average molecular weight in the range of about 400 to about 10,000.00 where n=2 to about 50
   (b) Optional Polytrimethylene ether glycol having a number average molecular weight in the range of about 1,000 to about 4,000,000 where n=11 to about 46.
   (c) Optional Polyethylene oxide having a number average molecular weight in the range of about 18,000 to about 2,000,000 where n=375 to about 41,667
   (d) Acid moieties are represented by the addition of dimethylol propionic acid
   (e) Glycidyl moieties are represented by the addition of glycidol
   (f) Urea moieties are represented by the addition of adipic acid dihydrazide
   (g) Excess isocyanate can react with dimethylol propionic acid to form an amide resulting in a urea
7. A composition comprising epoxy urethane urea (based off water addition) carboxylic acid alkylene oxide reactive coating compositions of the following structure (IV):



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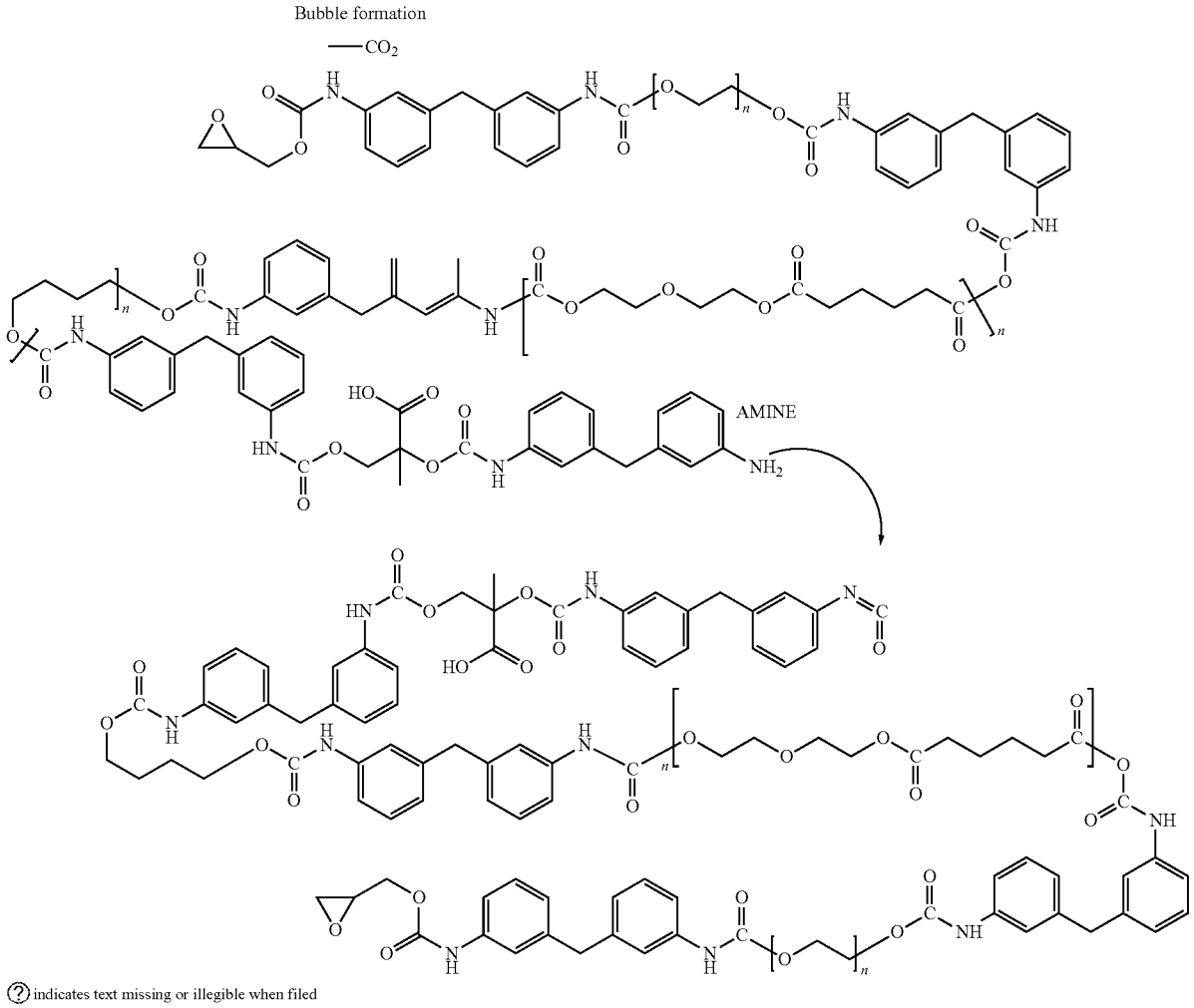
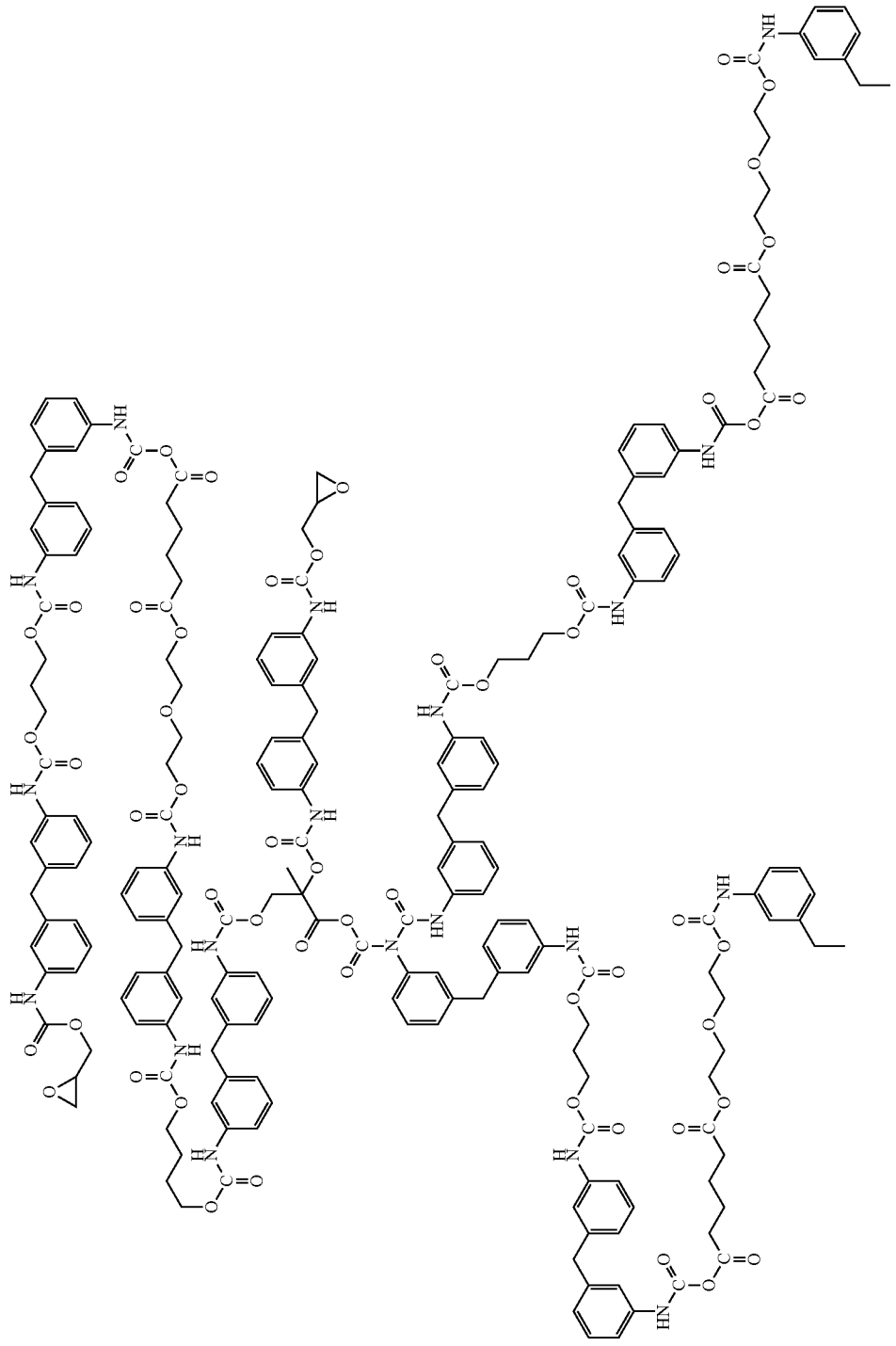


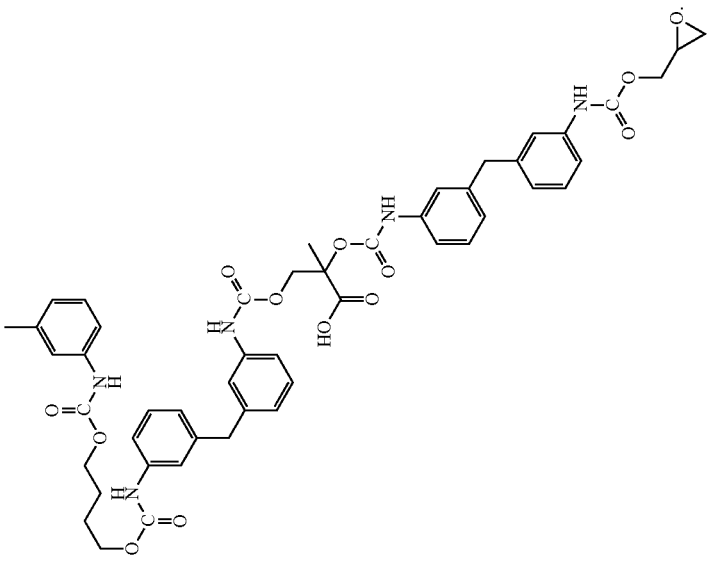
(?) indicates text missing or illegible when filed

8. The composition of paragraph 7, wherein the epoxy urethane urea carboxylic acid alkylene oxide reactive coating compositions are:
   (a) Poly[di(ethylene glycol) adipate having a number average molecular weight in the range of about 400 to about 10,000.00 where n=2 to about 50
   (b) Optional Polytrimethylene ether glycol having a number average molecular weight in the range of about 1,000 to about 4,000,000 where n=11 to about 46.
   (c) Optional Polyethylene oxide having a number average molecular weight in the range of about 18,000 to about 2,000,000 where n=375 to about 41,667
   (d) Acid moieties are represented by the addition of dimethylol propionic acid
   (e) Glycidyl moieties are represented by the addition of glycidol
   (f) Urea moieties are represented by the addition of reduced isocyanate system then adding water

9. A composition comprising epoxy urethane urea (based off excess iscoyanate) carboxylic acid alkylene oxide reactive coating compositions of the following structure (V):

(V)





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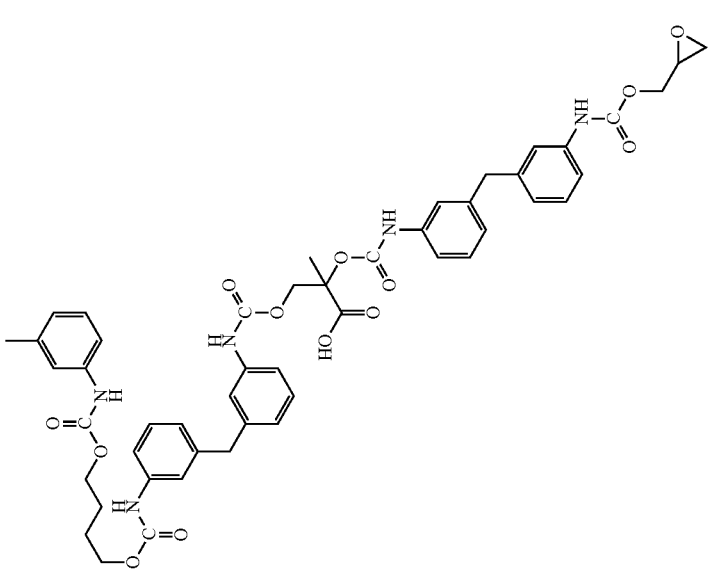
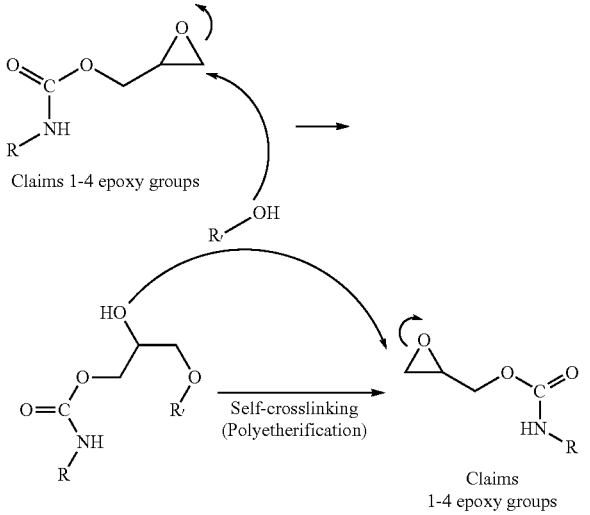
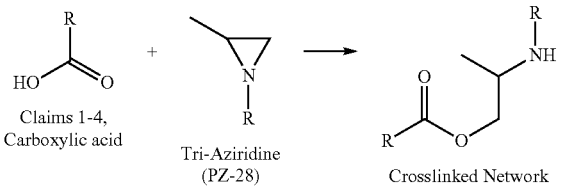


10. The composition of paragraph 9, wherein the epoxy urethane urea carboxylic acid alkylene oxide reactive coating compositions are:
    (a) Poly[di(ethylene glycol) adipate having a number average molecular weight in the range of about 400 to about 10,000.00 where n=2 to about 50
    (b) Optional Polytrimethylene ether glycol having a number average molecular weight in the range of about 1,000 to about 4,000,000 where n=11 to about 46.
    (c) Optional Polyethylene oxide having a number average molecular weight in the range of about 18,000 to about 2,000,000 where n=375 to about 41,667
    (d) Acid moieties are represented by the addition of dimethylol propionic acid
    (e) Glycidyl moieties are represented by the addition of glycidol
    (f) Urea moieties are represented by the addition of excess isocyanate, in the system, to adipic acid dihydrazide
11. An aqueous soluble or solvent soluble or mixture comprising claims paragraphs 1-10.
12. A composition of paragraph 11, where an aqueous soluble solvent is water and solvent soluble solvents are aprotic.
13. A composition of paragraph 12, where the aprotic solvents are NMP, DMSO or DMF.
14. A composition of paragraph 11, where the solvent can be a polar non-reactive solvent
15. A composition of paragraph 14, where the solvent can be PMA, Acetone or MEK.
16. A composition of paragraphs 1-10 where a chain extender is added.
17. A composition of paragraphs 1-10 where the curing agent is a self-crosslinking reaction via homopolymerization or polyetherification.

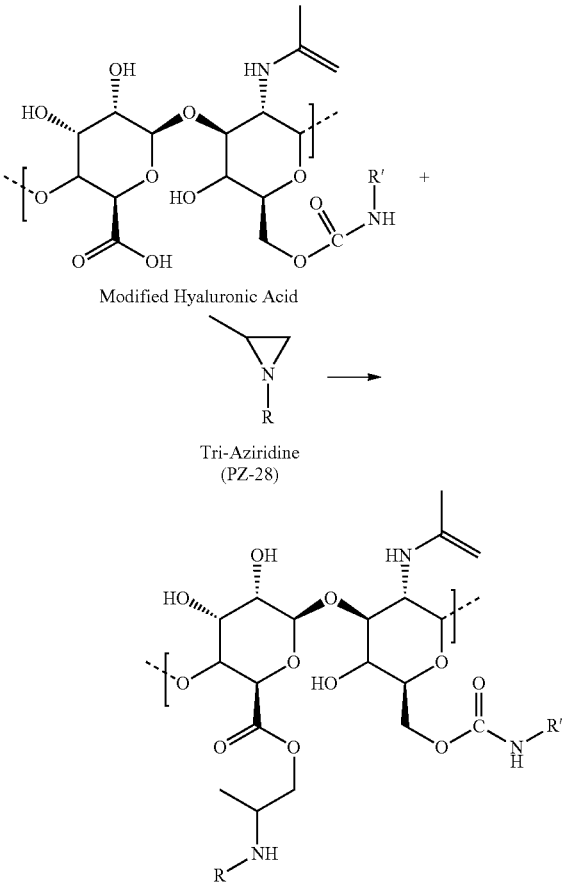


18. A composition of paragraph 17, where kinetics of the reaction are improved with temperature
19. A composition comprising a mixture compounds with structures (I), (II), (III), (IV) and (V)
20. A coating composition of paragraphs 1-10 further comprising a curing agent
21. A coating composition of paragraphs 3-10, wherein the curing agent is an aziridine curing agent
22. A composition of paragraph 21, where basecoat carboxylic acid groups can react with polyaziridine (PZ-28 or PZ-33):

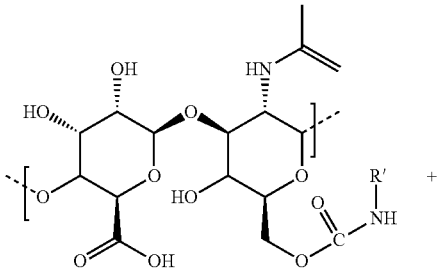


a) Polyaziridine PZ-28 reaction with basecoat (paragraph 22):

b) Polyaziridine PZ-28 or PZ-33, added to basecoat (paragraphs 3-10), reacts with carboxylic acid in modified Hyaluronic Acid topcoat:

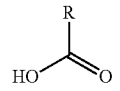


c) Polyaziridine PZ-28 or PZ-33 (paragraph 22), connecting basecoat to modified Hyaluronic Acid topcoat:

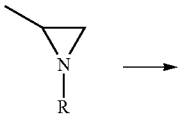


Modified Hyaluronic Acid

+



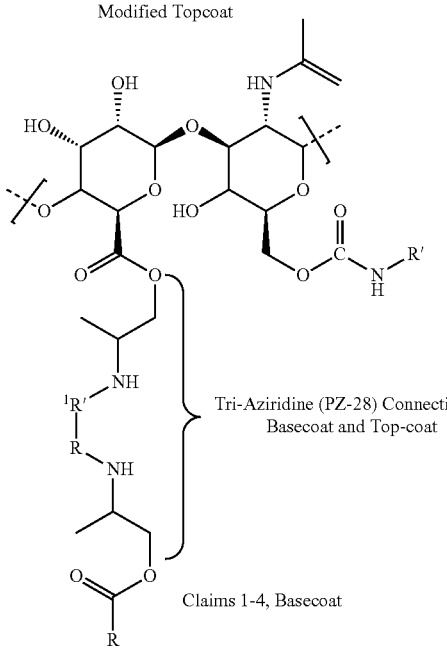
Claims 1-4, Carboxylic acid



Tri-Aziridine
(PZ-28)

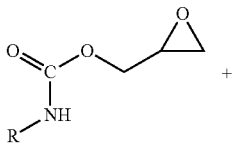
-continued

Modified Topcoat



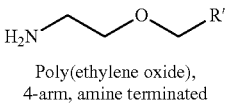
Crosslinked modified Hyaluronic Acid with Poly-Aziridine
(PZ-28)

23. A composition of paragraphs 1-10, where epoxy groups can react with an amine cross-linking agents (Figure below).



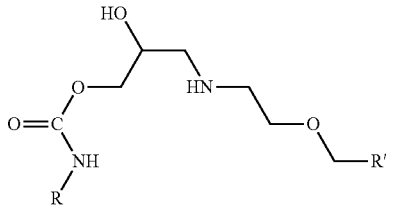
Claims 1-4 epoxy groups

+



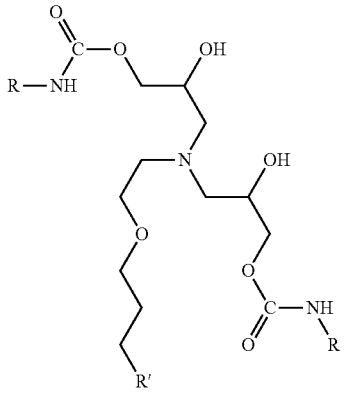
Poly(ethylene oxide),
4-arm, amine terminated

Primary amine reaction
with polyurethane epoxy



Primary amine

Secondary Amine reaction
with polyurethane epoxy

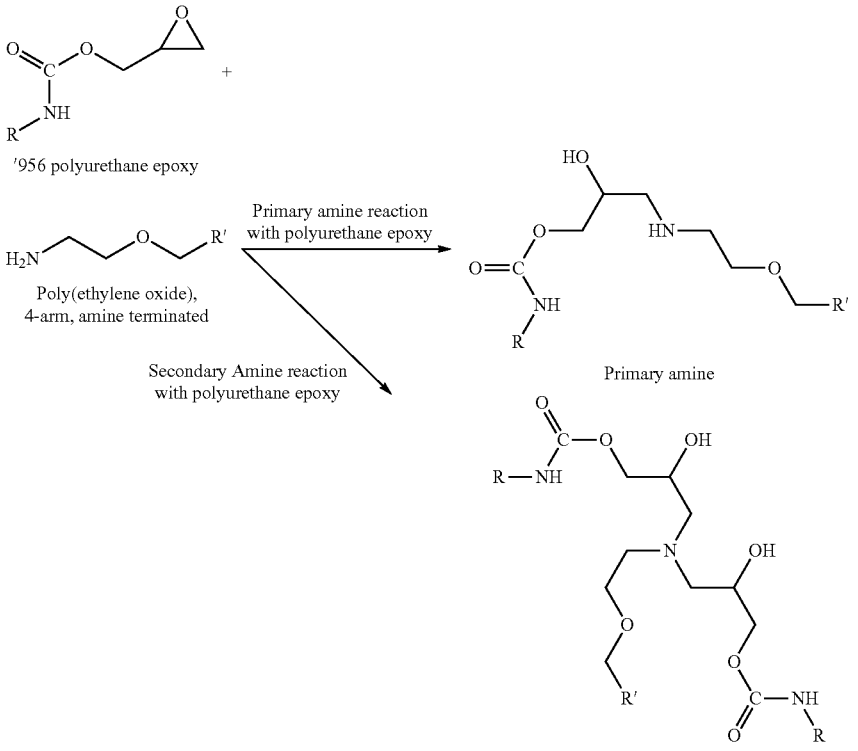


24. The coating composition of paragraph 23, wherein the amine curing agent is Poly(ethylene oxide), 4-arm, amine terminated

25. Basecoat epoxy groups can react with Poly(ethylene oxide), 4-arm, amine terminated found in topcoat.
    a. The '956 patent epoxy groups can react with Poly(ethylene oxide), 4-arm, amine terminated and Poly(ethylene oxide), 4-arm, amine terminated can react with basecoat to increase adhesive strength.

26. A composition of paragraphs 1-10, where open hydroxyl groups from epoxy group ring opening can react with isocyanate cross-linking agents (Figure below).

27. The coating composition of paragraph 26, wherein the isocyanate curing agent is Easaqua XM-502
    a) Easaqua XM-502 added to the basecoat reacts with basecoat carboxylic acid:



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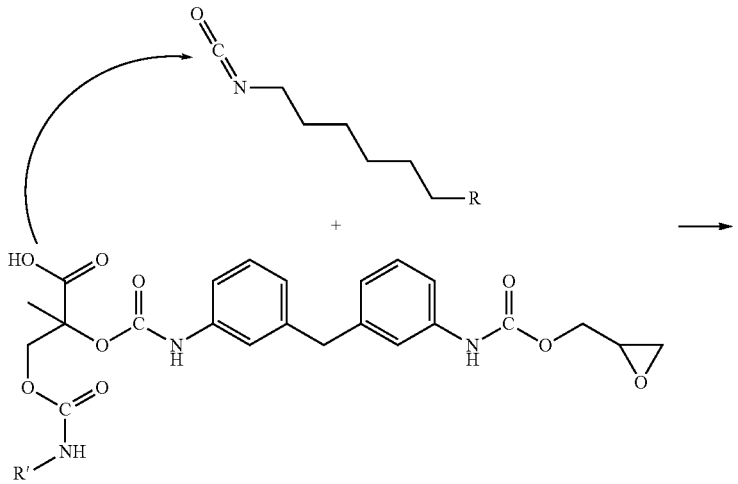

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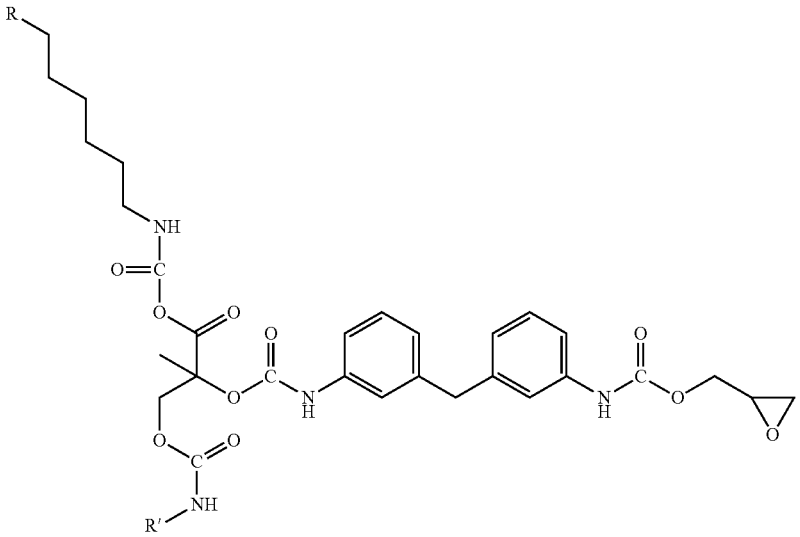
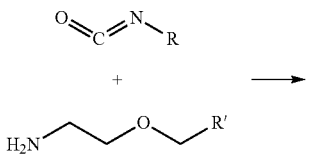


b. Easaqua XM-502 added to the basecoat reacts with Poly(ethylene oxide), 4-arm, amine added as a crosslinker to the top-coat:



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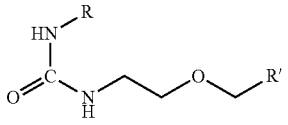
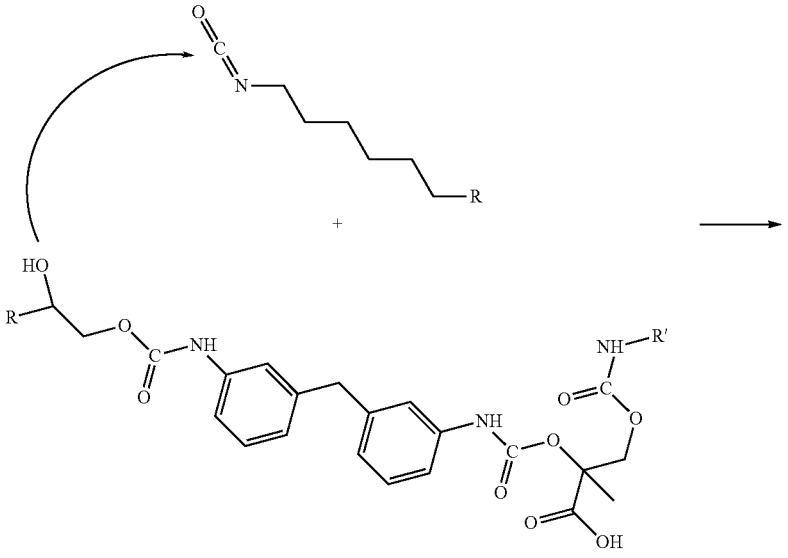


c. Easaqua XM-502 added to the basecoat reacts with open hydroxyls when the base-coat epoxy ring opens:



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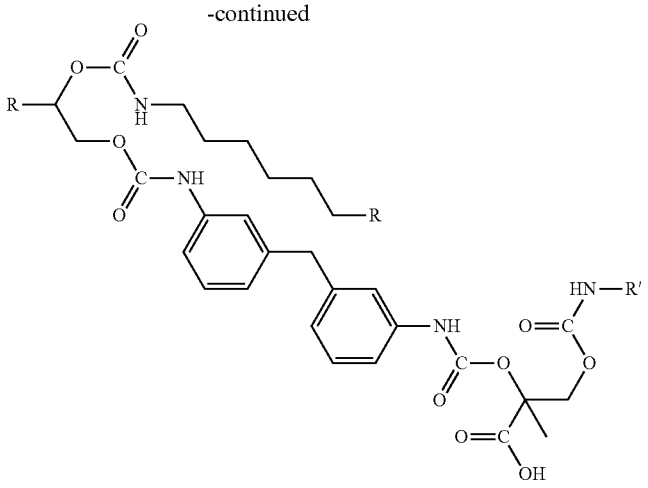
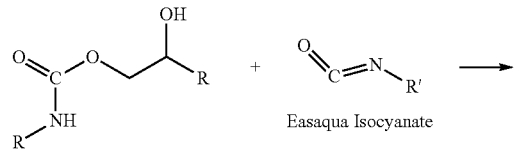
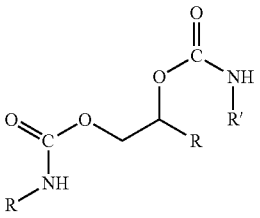


d. Easaqua XM-502 added to the basecoat reacts with open hydroxyls when the '956 patent ring opens:

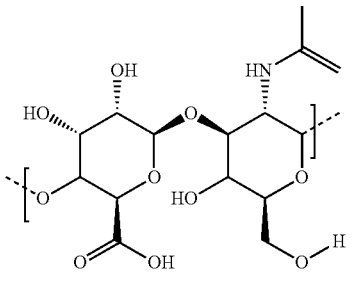


'956 polyurethane open epoxy with secondary hydroxyl

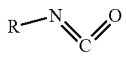
Easaqua Isocyanate



e. Easaqua XM-502 reacts with hydroxyl groups found in Hyaluronic acid:



Modified Hyaluronic Acid



Easaqua Isocyanate

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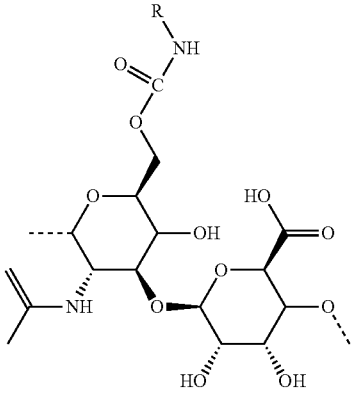
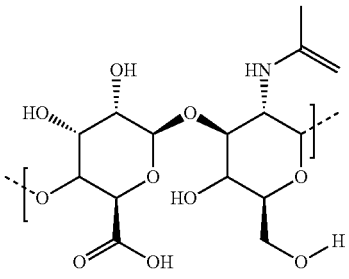
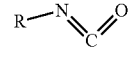


f. Easaqua XM-502 reacts with carboxylic groups found in Hyaluronic acid:



Modified Hyaluronic Acid



Easaqua Isocyanate

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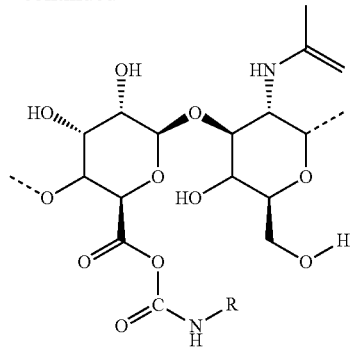
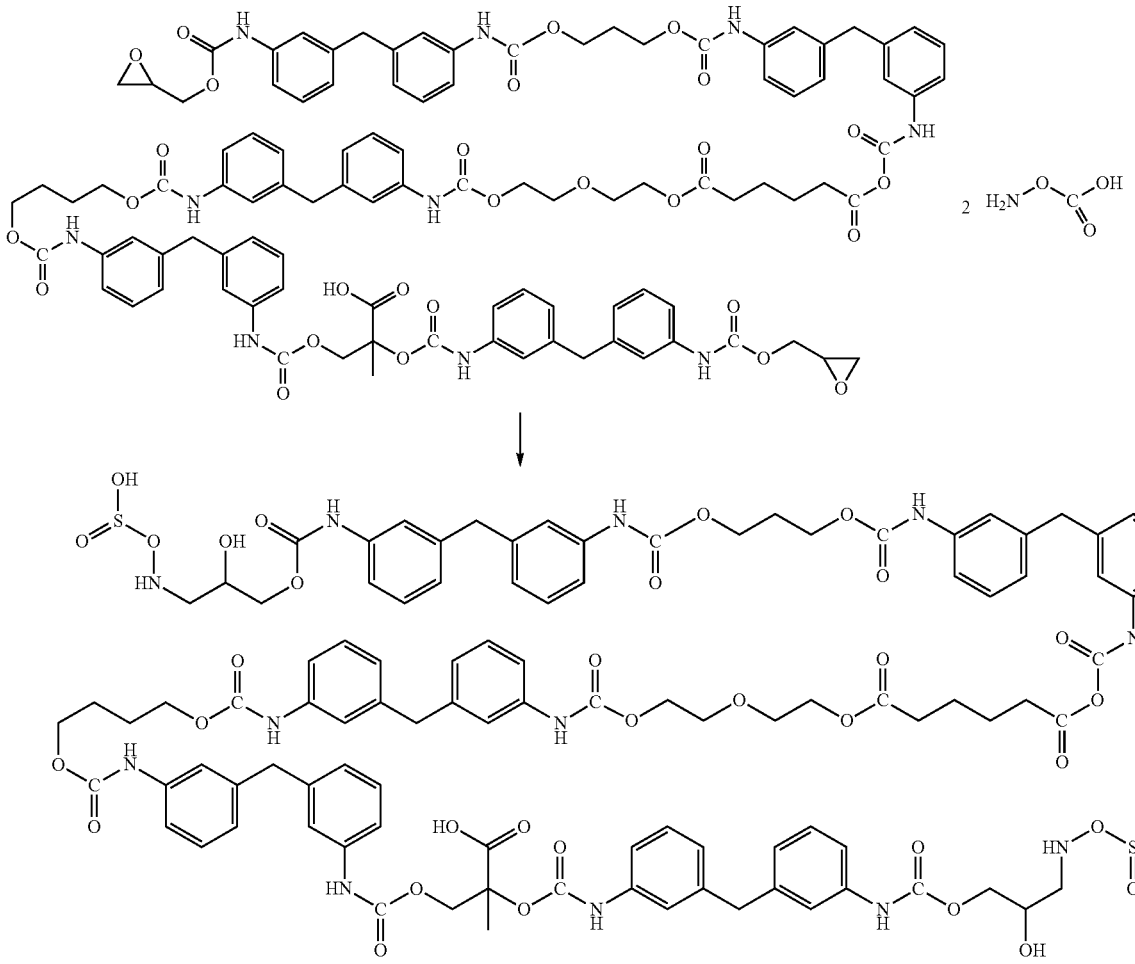


28. A composition of paragraphs 1-10, where epoxy groups can be end-capped with mono-functional amines:



29. A composition of paragraphs 3-10 where adding dimethylpropionic acid (DMPA) can lead to cross-linking sites and also help with water dispersion by forming water reducible epoxy polyurethanes.

30. A composition of paragraph 29, where acid groups of DMPA can be neutralized with an amine then dispersed in water.

31. A composition of paragraphs 1-10, where linear polyurethane epoxy polymers are elastomeric and can elongate.

32. A composition of paragraphs 1-10, where hydration forms a hydrogel via physical cross-links; or, slight cross-linking can cause a swelling (hydrogel formation) or plasticization effect resulting in a lubricious polyurethane end capped glycidyl based polymers.

33. Epoxy termination of paragraphs 1-10 may crosslink by amines, amides, carboxylic acids and hydroxyl functionality.

34. A coating composition of paragraph 33, where open hydroxyl functionality, from epoxy ring group opening, can undergo hydroxyl reactions.

35. A composition of paragraphs 1-10, are affected by diisocyanate type.

36. The coating composition of paragraphs 1-10, wherein the diisocyanate is selected from 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, 3,3'-dimethyl-4,4'-biphenyl diisocyanate, 4,4'methylene diphenyl diisocyanate, polymeric MDI, naphthalene diisocyanate, 4,4'-diisocynatodicyclohexylmethane, 1,4-benzene diisocyanate, trans-cyclohexane-1,4-diisocyanate, 1,5-naphthalene diisocyanate, 1,6-hexamethylene diisocyanate, 4,6-xylene diisocyanate, isophorone diisocyanate, with combinations and isomers thereof.

37. A composition of paragraphs 1-10, are reacted with polyol cross-linkers.

38. A composition of paragraphs 1-10, are reacted with amine cross-linkers.

39. A composition of paragraphs 5-10, where a diol or amine chain extender is added.

40. The coating composition of paragraph 20, wherein the diol chain extender is selected from hydroquinone-bis-(hydroxymethyl)ether, ethylene glycol, 1,2-propylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol, 2-methyl-1,3-propanediol, 3-methyl-1, 5-pentanediol, 2,2-dimethyl-1,3-propanediol, 2,2,4-trimethyl-1,5-pentanediol, 2-methyl-2-ethyl-1,3-propanediol, 1,4-bis(hydroxyethoxy)benzene, bis(hydroxyethylene) terephthalate, hydroquinone bis(2-hydroxyethyl)ether, and combinations and isomers thereof.

41. The coating composition of paragraph 20, wherein the amine chain extender is selected from 2,4 and 2,6 diethtl-toluene diamine, methylene-bis-orthochloroaniline, unilink (UOP LLC), 4,4'-methylene-bis(3-chloro-2,6-diethylaniline), 1,2-ethylenediamine, 1,6-hexanediamine, 1,2-propanediamine, 4,4'-methylene-bis(3-chloroaniline), dimethylthiotoluenediamine, 4,4'diaminodiphenyl-methane, 1,3-diaminobenzene, 1,4-diaminobenzene, 3,3'dimethoxy-4,4'-diaminobiphenyl, 3,3'-dichloro-4,4'-diamino biphenyl, and combinations and isomers thereof.

42. Paragraph 36 isocyanate selection, and isomers, affect physical crosslinks of the final epoxy terminated polyurethane polymer.

43. A coating composition of paragraph 42, where 4-4'MDI terminated epoxy polyurethanes provides excellent hard block domains due to linearity and aromatic groups.

44. A coating composition of paragraph 42, where isocyanate isomers of 2-4-TDI and 2,6-TDI react differently and impart different resin properties of the terminated polyurethane epoxy.

45. A coating composition of paragraph 36, where isocyanate crosslinkers can react with open hydroxyl functional groups (epoxy ring opening) to improve durability.

46. A composition of paragraphs 1-10, where pre-polymers can be made first then terminated with glycidol.

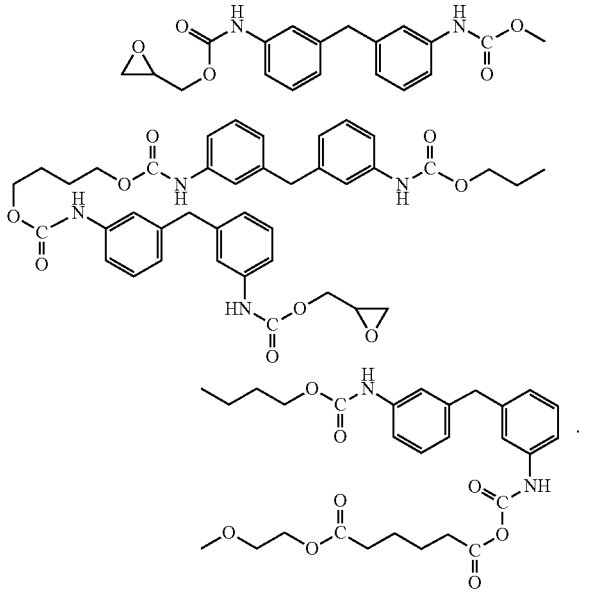
47. A composition of paragraphs 1-10, where a one shot synthesis can be used with all monomers, including glycidol, are added all at once.

48. A composition of paragraph 47, where monomers can be added to the reaction non-sequentially at any time during the reaction.

What is claimed is:

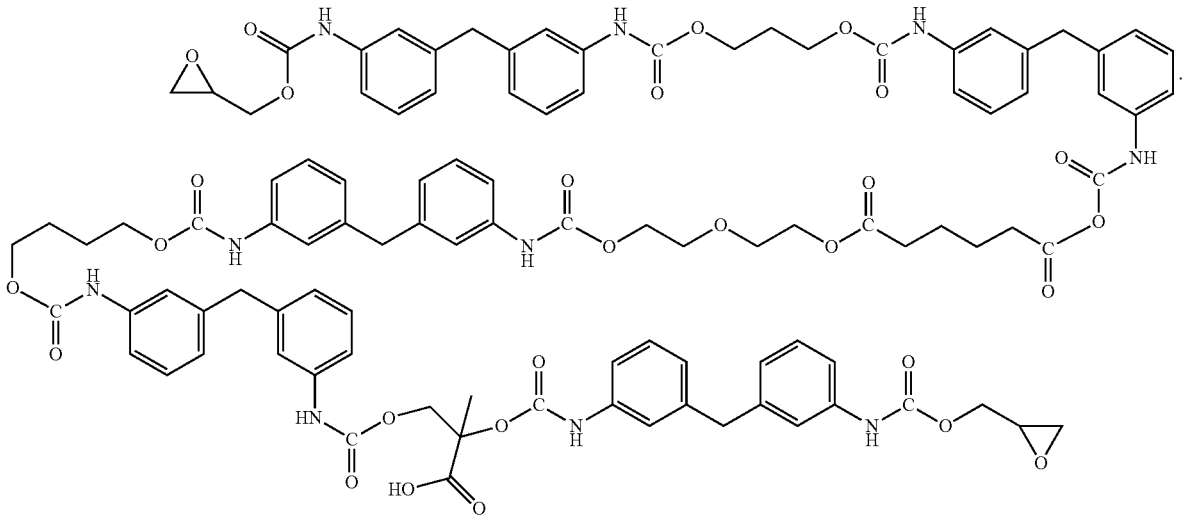
1. A composition comprising epoxy urethane alkylene oxide reactive coating compositions of the structure of formula (I)

(I)



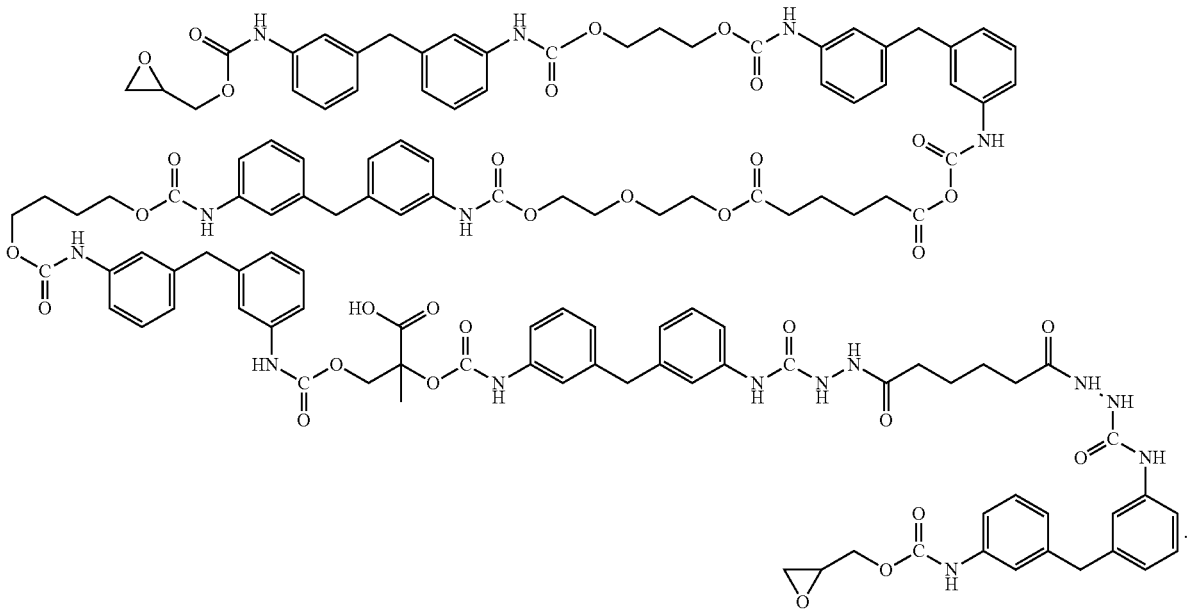
2. A composition comprising epoxy urethane ester carboxylic acid alkylene oxide reactive coating compositions of the following structure (II):

(II)



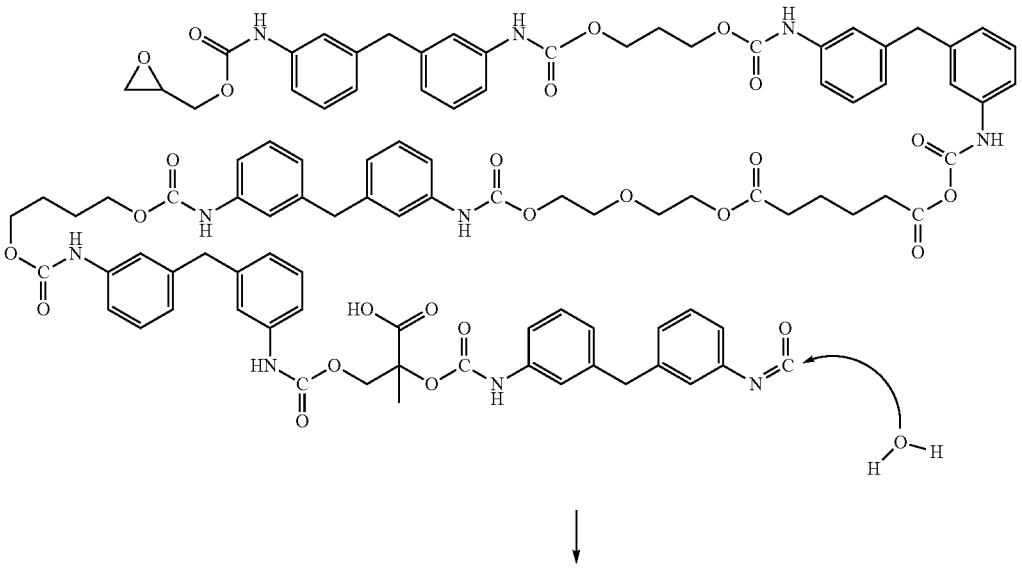
3. A composition comprising epoxy urethane urea carboxylic acid alkylene oxide reactive coating compositions of the following structure (III):

(III)



4. The product of the following reaction sequence (IV):

(IV)



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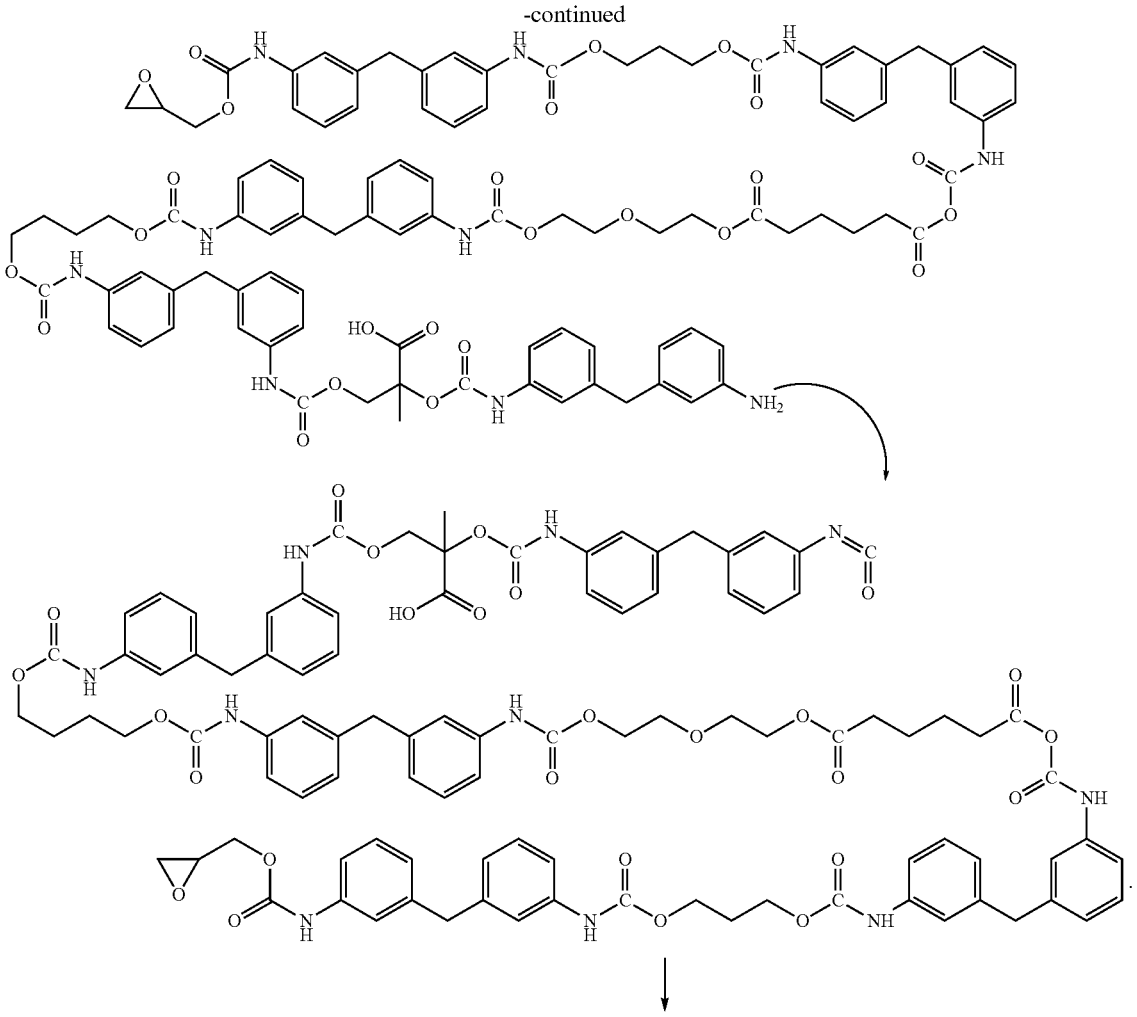
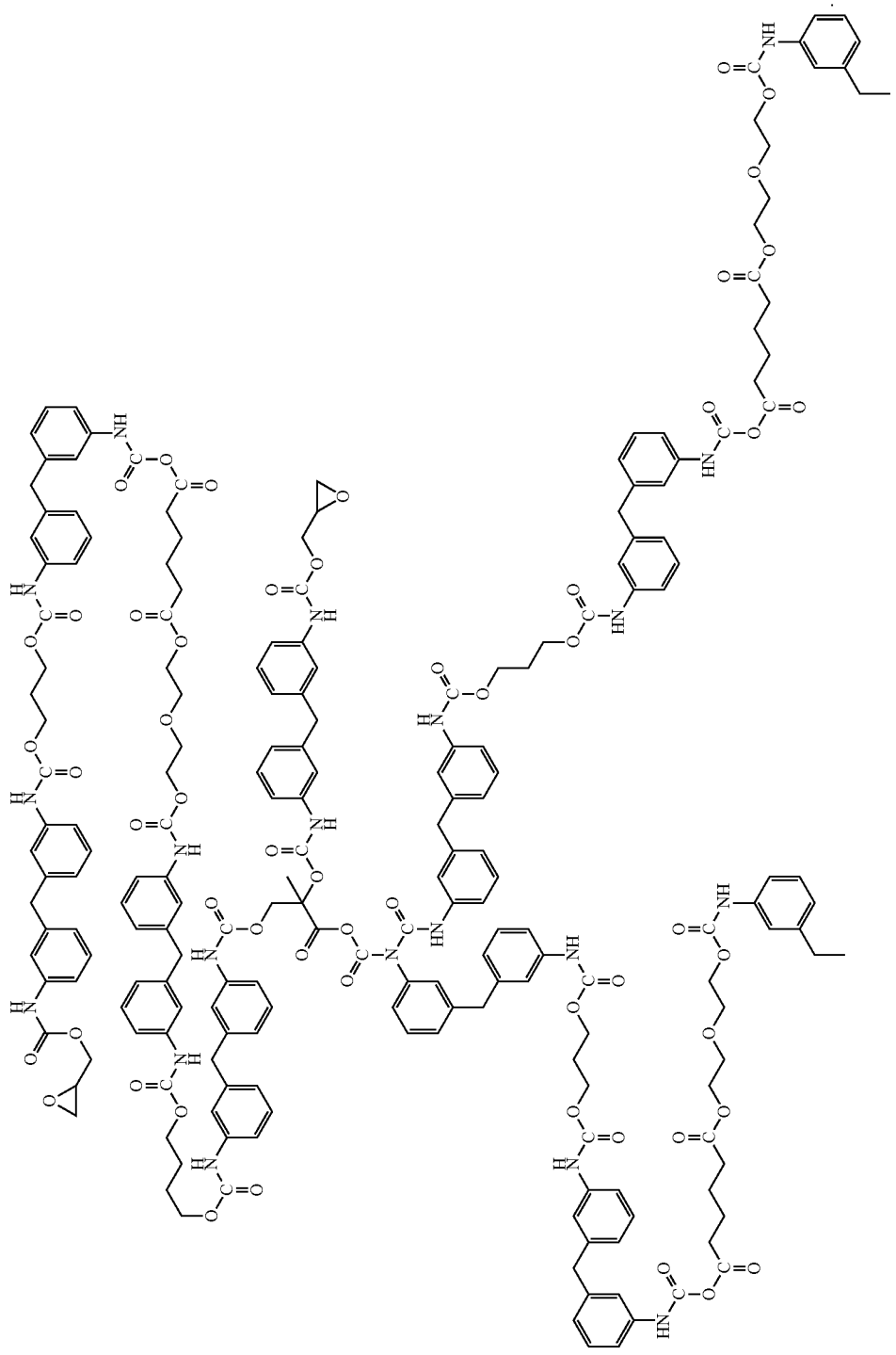
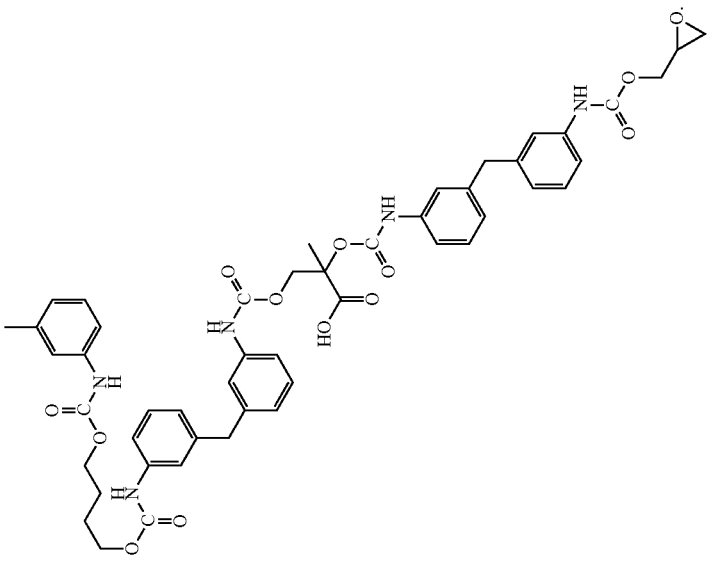


5. A composition comprising epoxy urethane urea amide carboxylic acid alkylene oxide reactive coating compositions of the following structure (V):

(V)





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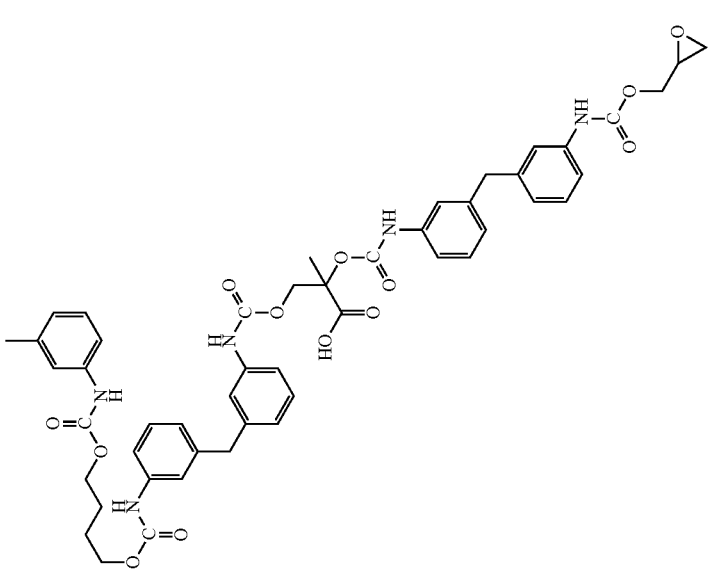
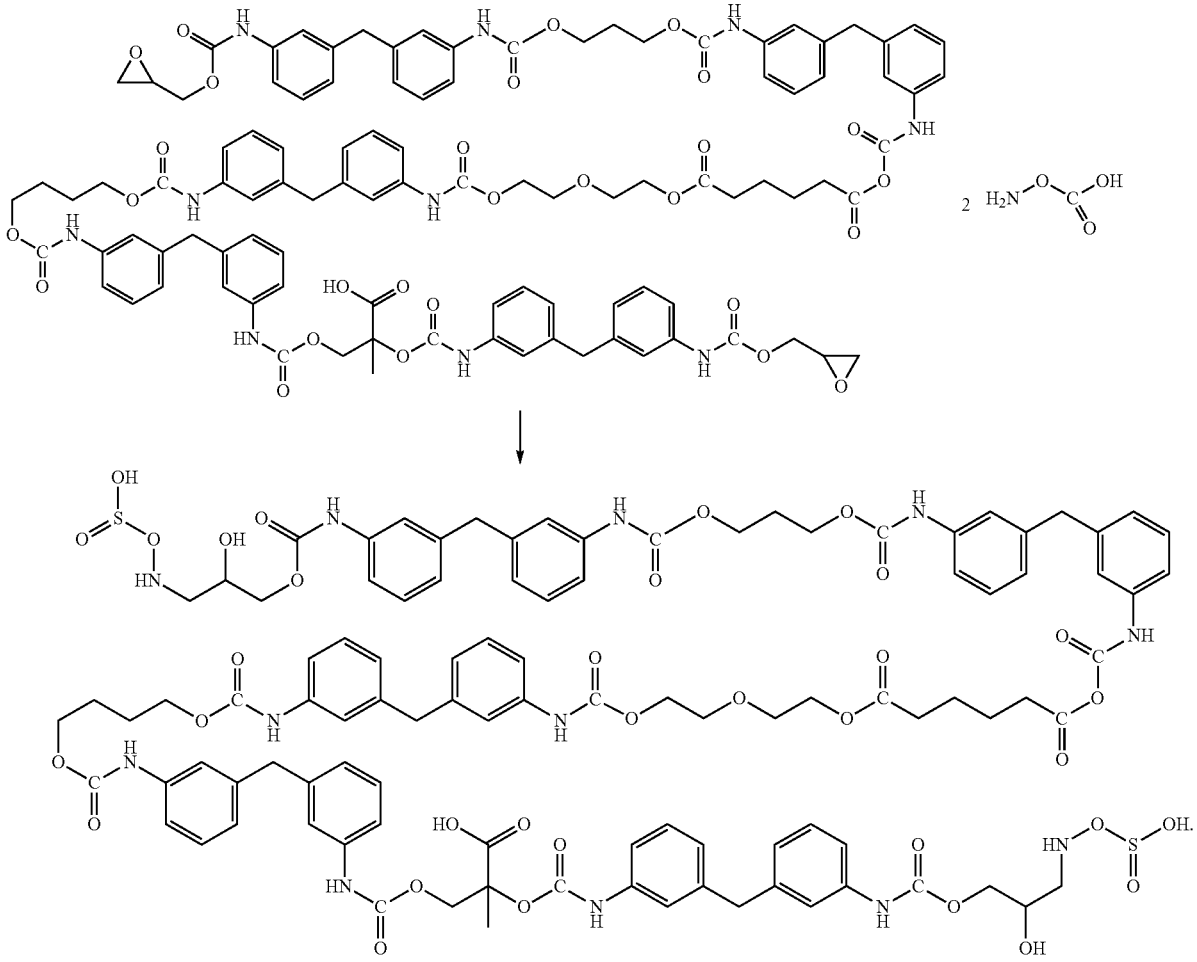


6. A composition prepared according to the following reaction sequence:



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